THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Volume XXV, No. 10

October, 1955

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

Copyright, 1956

CONSULTANTS BUREAU
259 West 14th Street
New York 11, N. Y.

Annual Subscription $ 95.00

Printed in the United States

Single Issue $ 20.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any article in this issue may be purchased from the publisher for $ 7.50

THE SYSTEM OF ATOMS*

G. P. Maitak

I. General Regularities

At the present time, when making a general survey of all the known stable and radioactive atoms, use is made of diagrams whose coordinates represent the atomic number (A) and the nuclear charge (Z) or magnitudes derived from these. Use is frequently made [1] of a diagram in which the coordinates are nuclear charge and isotopic number (the latter is the difference between the atomic number and the doubled charge of the nucleus), this was proposed by Harkins [2] as a "periodic of atomic species". In these diagrams the atoms with even Z were not segregated from those with odd Z. The system of atoms is more fully displayed by the enclosed table** in which the atoms with even and odd Z are segregated from one another.

Evenness and oddness of Z also plays a part in Mendelleev's periodic system of the chemical elements, but in the system of atoms its significance is greater. It suffices to refer to the experimental laws established by G. Oddo, W.D. Harkins, S. A. Shchukarev and others [3]. In the studies of G. Beck, H.L. Johnston, F. S. Sarkisov and others [4] on systematics, the atoms within a given group have one type of nuclear charge (even or odd) and constant isotopic number.

In the appended table the segregation of atoms with even and odd Z in the system of atoms acquires the same fundamental significance as does the division into even and odd series in D.I. Mendeleev's periodic system of the chemical elements. Mendeleev either separated the elements into even and odd series, expressing the periodic law in the form of a long table, or put them into subgroups and imparted to the law the form of a short table. Mendeleev's table can be regarded as composed of two tables – an odd and even – which are split up in the long table and inserted one in the other in the short table, but in such a way that the elements of the even and odd series present in one group are transferred to the subgroup.

The known regularities of properties of atoms entitle us also to regard the known diagrams of atoms (mentioned above) as composed of two diagrams – odd and even – depending upon the Z. In the known forms of diagrams they are inserted one in the other but in such a manner that the atoms of even and odd Z are not displaced; therefore the appended table of a "system of atoms", in which the even and odd atoms are segregated, is a more penetrating representation of periodicity. Its advantage is likewise the tabular form, which was adopted since the experiment of Mendeleev's periodic system of the chemical elements had demonstrated [6-8] the advantage of that table over various graphs and diagrams.

The structure and content of the table of the "system of atoms" (for brevity this will be subsequently referred to simply as the table or the system) are explained by the accompanying text.

In the table and in the diagram mentioned above [1] the stable atoms are bounded by radioactive atoms. The outer border of the bands of the table comprise atoms that emit electrons, and the inner border atoms that emit positrons; therefore in all groups in which there are no zones of relative stabilization, proceeding downwards, i.e. in the direction of increasing Z, also in the band of even Z from right to left and in the band of odd Z from left to right, i. e. in the direction of falling group number, at first we get β^--radioactive atoms, then stable atoms, and finally β^+- and (for heavy atoms) α-radioactive atoms.

---

* The usual name "system of atomic nuclei" is less acceptable. The other known term "system of isotopes" relates on the basis of the definition of isotopes to atoms of one element and to regularities in the pleiads.

** This table appears as a wall-chart and cannot be reproduced by Consultants Bureau.

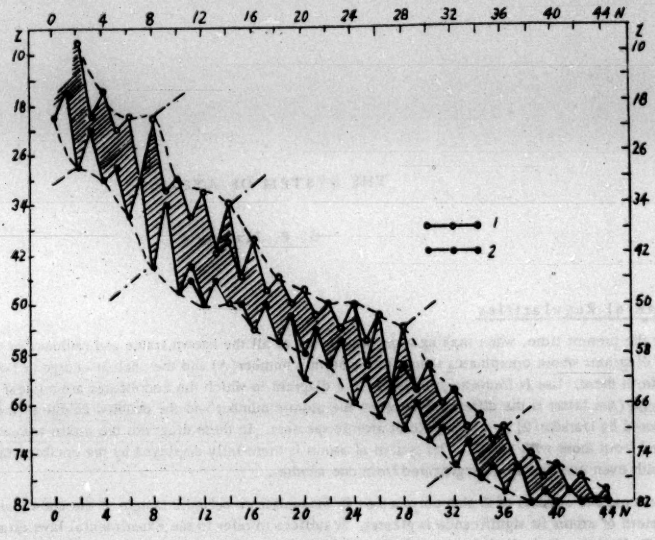


Fig. 1. Boundaries of stable atoms along the groups of the band of even Z. 1) upper boundary: lowest Z in group at which an atom is stable; 2) lower boundary: highest Z in the group at which an atom is stable.

But in the distribution of the stable and radioactive atoms and in the regularities of their properties along the axes of the coordinates in the table and in the diagram of [1], there is also a marked difference. It is caused by the asymmetry, which is noticeable side by side with the similarity, of the right and left bands of the table. In the right-hand band of the table the stable atoms form a dense field not split up by radioactive atoms (Fig. 1). In the left-hand band, however, the number of stable atoms is considerably smaller, and small groups of them and some isolated members are separated from one another by radioactive atoms (Fig. 2); also in the diagram of [1], therefore, which is constructed by combination of the right and left bands of the table, the stable atoms do not form a dense field but are interspersed with a radioactive atoms.

The general direction of the stable atoms is expressed, as seen from Figs. 1 and 2, by an equality of the hyperbolic type, but the boundaries of the field of the stable atoms in the band with even Z have conspicuous troughs and peaks due to the special zones of stabilization in the system of atoms.

The table and Figs. 1 and 2 also show that the range of values of Z within which the atoms are stable is greater with even Z in the even groups, while with odd Z it is greater in the odd groups. In the band of even Z in each even group the upper boundary of the stable atoms is in the region of lower values of Z, and the lower boundary is in the region of higher values of Z than in the neighbouring smaller and larger odd groups. This regularity is also observed in the change of the lower boundaries of the β^--radioactive atoms and of the upper boundaries of the β^+-radioactive atoms when passing along the groups of the right-hand band of the table (Fig. 3). The converse is the case in the distribution of the stable atoms and in the boundaries of the β-radioactive atoms in passing along the groups of the left-hand band (odd Z) of the table (Figs. 2 and 4).

The diagram of [1], in which the right and left bands of the table are combined, naturally could not reveal these regularities.

A similar regularity is observed in the change throughout the groups of the table of the abundance of the atoms; as already reported [2, 11], the abundance is a function of the evenness or oddness of their isotopic number and their mass in the case of even and odd Z.

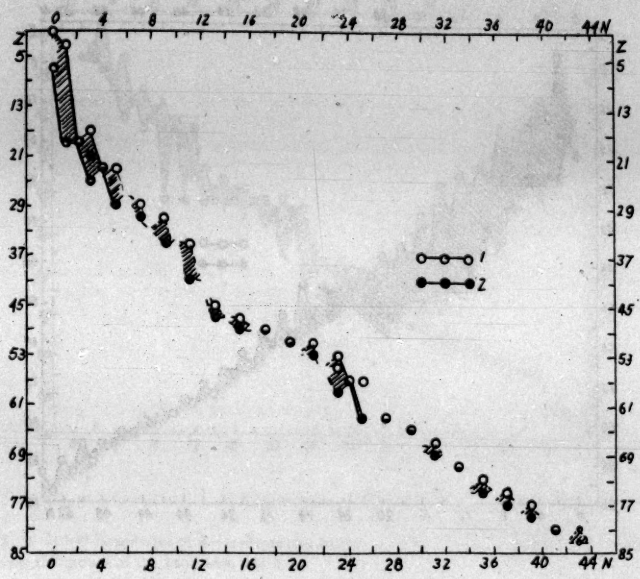


Fig. 2. Boundaries of stable atoms along groups of band with odd Z.
1) upper boundary: lowest Z in group at which an atom is stable; 2) lower boundary: highest Z in group at which atom is stable.

These regular changes of properties of atoms through the groups of the table are caused by a corresponding change of the stability of the atoms through the groups. This is evident on comparing these regularities with the changes in the mass defects of the atomic nuclei in passing along the groups of the table. With a few exceptions the bond energy of nuclear particles in the band of even Z values is greater in the even groups than in the neighbouring odd groups, while in the band of odd Z values, conversely, the energy is greater in the odd groups than in the neighbouring even groups. Judging by the magnitudes of the total defects of masses of the nuclei Δ (determined as the difference between the mass of the individually taken neutrons and protons constituting the nucleus and its exactly measured mass), this regularity is not very conspicuous. It is better appreciated from the change from group to group of the table of the ratio of the mass defect of the nucleus to the mass number . Δ/A, the mass defect of the nucleus per nucleon. However, even in changes of mass defects by 1 nucleon, this regularity is manifested only in light nuclei, while in heavier nuclei it is insig ificant. Moreover the observed serrated character of the boundaries of the stable and the β-radioactive atoms from group to group of the table, bound up with a similar course of the change of their stability through the groups, is clearly reflected (see Figs. 1-4) also in the region of heavier atoms. This is because the difference in the stability of each of the two isotopes in neighbouring groups of one series is governed by the mass defect, and the latter in turn is governed by the addition of one neutron, while for calculation of the ratio Δ/A this mass defect is spread over all the nucleons of the nucleus, and therefore in heavier nuclei (in which the number of nucleons is large) this difference is no longer reflected by the magnitudes of Δ/A. But the difference in the total mass defects of nuclei of each of the two isotopes in neighbouring groups of one series equal to the mass defect brought about by addition of the last neutron to the nucleus of each prededing group with formation of the nucleus of each given group of the same series actually changes from group to group of the table right down to the heaviest nuclei for which the mass of the atoms is known accurately, in complete correspondence with the described other changes in nuclear properties along the groups. In the band with even Z (Fig. 5) the mass defect of each nucleus of each

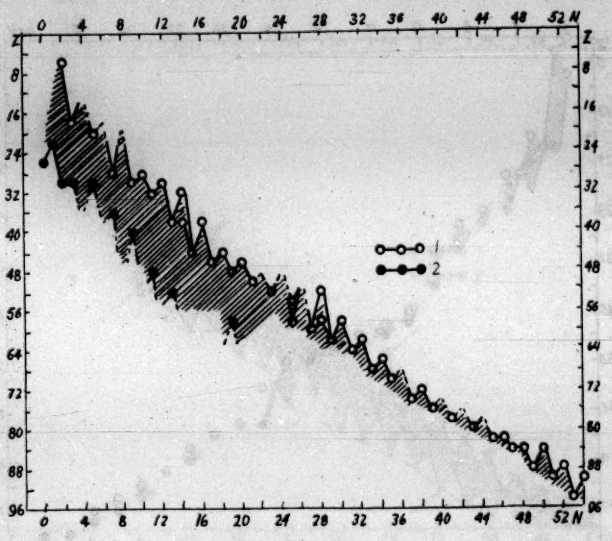


Fig. 3. Lower boundaries of the β^--radioactive and upper limits of the β^+-radioactive atoms along the groups of the band with even Z.
1) Lower boundary of β^--radioactive atoms in the group: highest Z in the group at which an atom is β^--radioactive; 2) upper boundary of β^+-radioactive atoms in the group: lowest value of Z in the group at which an atom is β^+-radioactive.

the mass defect of the succeeding nucleus of the same series present in the odd group exceeds its mass defect. Conversely in the band of odd Z values (Fig. 6), in the majority of cases the mass defect of each given nucleus of each odd group exceeds the mass defect of the preceding nucleus of the same series present in the even group, by a greater amount than the mass defect of the succeeding nucleus of the same series present in the even group exceeds its mass defect.

The properties of the atoms also change in a regular manner in the vertical direction in the groups of the table from series to series.

On arranging the atoms of equal values of $A-2Z$ in the order of increasing Z, without segregation of even and odd Z as in the aforementioned diagram of [1], the stable atoms frequently alternate with radioactive atoms, while in the case of radioactive atoms the half-life period and the energy of the emitted particles do not change monotonically. In contrast with this, in the groups of the table, the stable β^-- and β^+-radioactive atoms are not mixed, but form uniform aggregates of respectively the middle, upper and lower series of the groups. The only exceptions are in six groups of the band of even Z and in four groups of the band of odd Z in which the uniformity of the components of the radioactive atoms is upset by the stability of Ca^{48}_{20}, Se^{82}_{34}, Kr^{86}_{36}, Ba^{137}_{56}, Xe^{136}_{54}, Sm^{144}_{62}, Nd^{143}_{60}, Sm^{147}_{62}, Y^{89}_{39}, Pr^{141}_{59}, La^{138}_{57}, La^{139}_{57}. But this is because the atoms in question occur in special stabilization zones. Outside these special zones the groups of the table are characterized by regularity not only of distribution and uniformity of components of the stable and radioactive atoms, but also of the properties of the atoms in the groups. Thus, within the limits of each group the half-life period falls off, while the maximum energy of the emitted particles increases in the case of β^--radioactive atoms from bottom to top in the direction of decreasing Z, and in the case of β^+-radioactive atoms from top to bottom in the direction of increasing Z. In some groups these changes are satisfactorily formulated by simple expressions. Thus, for example, the maximum energy of the positrons emitted by radioactive atoms

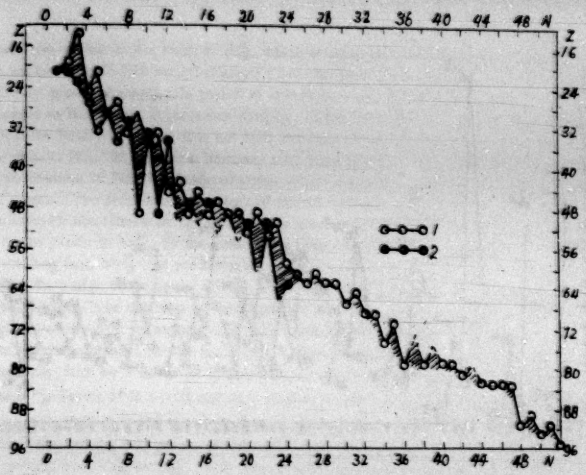


Fig. 4. Lower boundaries of β^--radioactive atoms and upper limits of β^+-radioactive atoms along the groups of the band with odd Z.
1) lower boundary of β^--radioactive atoms in the group: highest Z in the group at which an atom is β^--radioactive; 2) upper boundary of β^+-radioactive atoms in a group: lowest Z in group at which an atom is β^+-radioactive.

of groups −1 and zero of odd Z and of groups −1 and 5 of even Z is expressed respectively by the following linear functions of Z, the coefficients of which were determined from experimental values of the maximum energy by the method of least squares: $E = 0.2680 \cdot Z - 0.4799$, $E = 0.5093 \cdot Z - 3.8797$, $E = 0.2846 \cdot Z - 0.6057$, $E = 0.2155 \cdot Z - 6.0241$. For β^+-radioactive atoms of groups −2, −1, 1 and 5 of the band with even Z and those of group −1 with odd Z, the product of the half-life period and the fifth power of the maximum energy of the emitted positrons scarcely varies within a group.

A study of the general regularities of the table of the system of atoms also revealed that in all the groups the bands with even Z (N = −2, −1, 0, 1, 2, 3, 4, 5, 6, 8) and odd Z (N = −1, 0, 1, 2, 3) in which there are more than two atoms whose masses have been accurately measured [12] up to the time of the present investigation, the magnitudes of the total mass defects of the nuclei Δ are approximately a linear dependence on Z within a given group; we may therefore suggest that this is a general law. On the basis of this law, group empirical equations were obtained for calculation of the masses of atoms in the groups of the table; these expressions give approximately parallel straight lines equidistant from one another and therefore reduce to more general equations [13]. These equations are cited in the table.

II Zones of Stabilization

Atoms whose properties deviate from the general laws described above for the groups and series of the table form zones of stabilization in the system of atoms.

Most of these deviations are caused by three out of the four zones of stabilization, and these lead to a peak in the upper and a trough in lower boundaries of the stable atoms of the even groups of the right-hand band of the table (Fig. 1). In the table the assemblies of atoms encompassed by these zones are separated. A characteristic feature is the concordance of those data about these zones that give the boundaries of the stable and β-radioactive atoms in the groups of the table, the half-life period of the radioactive atoms, the abundance of stable atoms and the position of the most abundant atoms of groups and series.

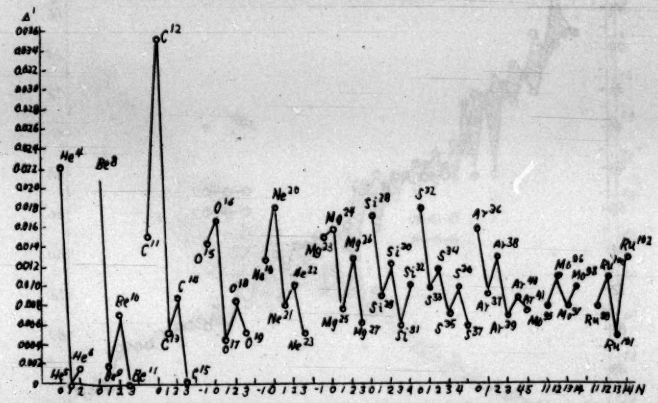


Fig. 5. Mass defect on formation of nucleus X_Z^A by addition of one neutron to nucleus X_Z^{A-1} in the case of even Z (difference of the total mass defects of nuclei X_Z^A and X_Z^{A-1} in the case of even Z).

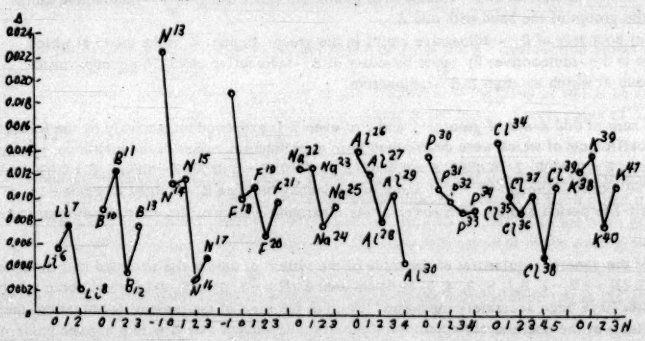


Fig. 6. Mass defect in formation of nucleus X_Z^A by addition of one neutron to nucleus X_Z^{A-1} in the case of odd Z (difference of the total mass defects of nuclei X_Z^A and X_Z^{A-1} in the case of odd Z).

All these properties point to a zone of stability in the direction from Ni_{28}^{58} to Ca_{20}^{48}. The stability of these atoms results in the first peak of the upper boundary (N = 8)* and the oppositely situated (in the direction of the broken curve of Fig. 1) trough of the lower (N = 2) boundary of the stable atoms of the even groups of the band with even Z. They also indicate the deviation from monotonic change in the groups of the table of the half-life period of radioactive atoms. In the 7th group, in passing from $Ni_{28}^{(54)}$ to Cr_{24}^{56} the half-life period decreases, but subsequently, in passing to Ti_{22}^{51}, it does not decrease but increases, and it is still high at $Ca_{20}^{(47)}$, although shorter than in the case of Ti_{22}^{51}. In the 9th group Ca_{20}^{48}

* Here and in subsequent similar cases the reference is to the number of the group in the table of a system of atoms as well as to the axis of the abscissas of Fig. 1.

has the same half-life period as the atom of Ni^{66}_{28}, which is considerably more distant from it, whereas in the groups lacking special zones the half-life period changes more rapidly with change of Z. In the case of the β^+-radioactive atoms of the 1st group, the half-life period at first falls in the direction of heavier atoms but later, on transition to Ni^{57}_{28} (located in this zone), it increases sharply. In the 3rd group on passing from Cr^{51}_{24} to Fe^{55}_{26} and Ni^{59}_{28} (present in this zone), the half-life period does not fall, and only in the case of the succeeding atoms in conformity with the general law does it fall. In complete harmony with what has been said, the indications of this and other zones of stabilization give changes in the abundance of stable atoms and once again illustrate the relation between abundance and stability of atoms. The predominating atom of the 8th group is Ni^{64}_{28}. The special position of Ca^{48}_{20} in the abundance data results in its abundance being considerably greater than that of the remaining atoms of this group which includes those atoms closer to Ni^{64}_{28}. In the case of the atoms of the second group positioned in the table in the downward direction starting from Ne^{22}_{10} (the predominating atom in this group), the abundance declines as far as Ti^{46}_{22}, but then rises and reaches a high value again at Fe^{54}_{26}, which corresponds to the second maximum of abundance in the groups, and at Ni^{58}_{28}, which is in the zone of stabilization. The same zone also contains Fe^{56}_{26}, (the predominating atom of the 4th group and of the iron series) and Cr^{52}_{24}, (the predominating isotope of chromium), as well as Cr^{53}_{24}, Ti^{46}_{22} and Ti^{50}_{22}. The three latter are present for the following reasons: On passing from the predominating isotope of chromium to Cr^{53}_{24} the abundance falls by a factor of 9, which is very much smaller than the fall on passing in the iron series from Fe^{56}_{26} to Fe^{57}_{26}, where the factor of fall is 42 and only slightly smaller than on passage in the titanium series from Ti^{48}_{22} to Ti^{49}_{22}, which is accompanied by a $13\frac{1}{2}$ times change in abundance. The atom of Ti^{50}_{22} causes a peak in the upper boundary of the stable atoms of the odd groups of the band with even Z (Fig. 1). The abundance declines to an insignificant extent on passing from Cr^{52}_{24} to Ti^{50}_{22}. With increasing Z the predominating isotopes of the pleiads, in conformity with the general direction of both bands of the table, are displaced in general to larger N, and to smaller N only in the zones of stabilization as, for instance, in passing from iron to nickel (see above). All the mentioned atoms of this zone lie in one direction with very similar values of Z + N ranging from 27 to 30 (average 28).

Atom	Ni^{57}_{28}	Ni^{58}_{28}	Fe^{54}_{26}	Fe^{55}_{26}	Fe^{56}_{26}	Cr^{52}_{24}	Cr^{53}_{24}	Ti^{49}_{22}	Ti^{50}_{22}	Ti^{51}_{22}	$Ca^{(47)}_{20}$	Ca^{48}_{20}	Ca^{49}_{20}
Z+N	29	30	28	29	30	28	29	27	28	29	27	28	29

Possibly this is only one branch of a complex pattern whose structure will become clear after a study of the properties of still unknown atoms which will broaden the bands of the system and after exact measurement of the masses of the possibly larger number of atoms. We may thus postulate a horizontal branching of the zone to the right from Fe^{54}_{26} and Ni^{57}_{28}. This postulate is based on the previous considerations regarding the atoms of Fe^{54}_{26}, Fe^{55}_{26}, Fe^{56}_{26}, Ni^{57}_{28}, Ni^{58}_{28}, Ni^{59}_{28} and Ni^{64}_{28}, namely the fact that corresponding to all the stable isotopes of iron is a maximum of the abundance curves of the atoms of the corresponding groups, so that the abundance at once falls sharply in the upward direction, whereas in the downward direction it only falls after the nickel series; a further consideration in support of the postulate is the increase in the half-life period on transition in the 9th group from Zn^{66}_{30} to Ni^{66}_{28}.

In the left hand band of the table this zone of stabilization has a direction similar to that described. Here the diagonal portion of the zone, encompassing the atoms with the same values of Z + N, is directed from atoms of Co^{55}_{27} and Co^{56}_{27} to Sc^{46}_{21} and Sc^{47}_{21}. This direction of the zone has the following implications: In the case of the specified β^+-radioactive atoms of cobalt, the half-life period is longer than that of the β^+-radioactive atoms of Mn^{51}_{25} and Mn^{52}_{25} respectively which, judging by their half-life periods and the half-life periods of the light β^+-radioactive atoms of the same groups, are also encompassed by this zone. The succeeding atom of Mn^{53}_{25} (in the same direction) evidently has a half-life period similar to that of $V^{(48)}_{23}$. In the vanadium series in this direction are V^{50}_{23}, the stability of which breaks into the consistently β^--radioactive atoms of the 4th group, and V^{51}_{23}, the most abundant vanadium isotope. Then follows Sc^{46}_{21}, the half-life period of which is longer than that of $V^{(47)}_{23}$, and Sc^{47}_{21}, whose half-life period is only a little shorter than that of Co^{61}_{27}. Consequently in the left band of the table the diagonal portion of this zone encompasses the following atoms:

Atom	Co^{55}_{27}	Co^{56}_{27}	Mn^{53}_{25}	V^{50}_{23}	V^{51}_{23}	Sc^{46}_{21}	Sc^{47}_{21}
Z + N	28	29	28	27	28	27	28

The horizontal offshoot of this diagonal portion of the zone, in the band of atoms of even Z, observed in the series of iron (Z = 26) and nickel (Z = 28), is here observed in the cobalt series (Z = 27). Apart from what was already said about the atoms of Co^{55}_{27} and Co^{56}_{27}, it is manifested in the similarity of the half-life periods of Co^{57}_{27} and $V^{(48)}_{23}$, and also in the facts that Co^{59}_{27} is the predominant atom of the group and that the half-life periods of Co^{60}_{27} and Co^{61}_{27} are longer than those of Cu^{64}_{29} and Cu^{66}_{29} respectively.

The second peak of the upper (N = 12, 14, 16) boundary and the oppositely situated trough of the lower boundary (in the direction of the broken line of Fig. 1) of the stable atoms of the even groups of the band of even Z indicate a zone of stabilization resulting in stability of Ge^{76}_{32}, Se^{82}_{34}, Kr^{86}_{36}, Mo^{92}_{42}, Ru^{96}_{44}, Pd^{102}_{46}, Cd^{106}_{48}, Sn^{112}_{50} and Zr^{96}_{40}. If no zone of stabilization had here existed, these atoms would have been radioactive, and the boundaries in question would have lacked the trough and peak responsible for their stability. The diagonal portion of this zone is made up of atoms with Z + N from 48 to 52 (average 50), arranged in the direction from Se^{82}_{34} and Kr^{86}_{36} (N = 14) to Mo^{92}_{42} and Ru^{96}_{44} (N = 8). In the 14th group the true upper boundary of the portion of stable atoms is Zr^{94}_{40}. It lies on a hyperbolic curve which may be drawn through the top of the boundary of the stable atoms of the 4th, 10th, 18th and other groups of the band of even Z (Fig. 1) located between the peaks resulting from the zones of stabilization. Following it upward in the same group is Sr^{90}_{38} which is β^--radioactive (although long lived), but after that the stability of the atoms in this group increases to such an extent that Kr^{86}_{36} and Se^{82}_{34} are no longer radioactive and Se^{82}_{34} is abundant in comparison with the other stable atoms of the 14th group. At the other end of the diagonal portion of this zone, in the region of atoms of Mo^{92}_{42} and Ru^{96}_{44}, relative stability is subsequently displayed. The stability of these atoms is marked by a peak of the lower boundary of the stable atoms of the 8th group. The abundance, which had fallen in the 8th group before these atoms, rises at Mo^{92}_{42}, while at Ru^{96}_{44} it declines but not sharply. In the case of the β^+-radioactive atoms of the 7th group, the half-life period starting from Se^{75}_{34} falls off with increasing value of Z in conformity with the general law, while on transition to Ru^{95}_{44} (located in this zone) it increases. In the 9th group the same is observed on transition from Zr^{89}_{40} to the atoms of Mo^{93}_{42} and Ru^{97}_{44} encompassed by this zone. In the 10th, 11th and 12th groups in the direction of the diagonal portion of the zone are found the atoms Zr^{90}_{40}, Zr^{91}_{40}, Zr^{92}_{40} and Sr^{88}_{38} which predominate in these groups. Sr^{88}_{38} and Zr^{90}_{40} also predominate in the series, and in going from strontium to zirconium the number of the group of the predominating isotope of the pleiad is shifted to lower values; this is observed (as already remarked) only in zones of stabilization. In the 13th group the half-life period of Kr^{85}_{36} is not shorter but longer than that of Sr^{89}_{38}. Thus the diagonal portion of this zone encompasses the following atoms:

Atom	Ru^{95}_{44}	Ru^{96}_{44}	Mo^{92}_{42}	Mo^{93}_{42}	Zr^{90}_{40}	Zr^{91}_{40}	Zr^{92}_{40}	Sr^{88}_{38}	Kr^{85}_{36}	Kr^{86}_{36}	Se^{82}_{34}
Z + N	51	52	50	51	50	51	52	50	49	50	48

The atoms of Pd^{102}_{46}, Cd^{106}_{48} and Sn^{112}_{50}, the stability of which gives rise to the trough in the lower boundary of the stable atoms of the 10th and 12th groups of the band of even Z (Fig. 1), form, as seen from the table, an offshoot of the described diagonal portion of the zone. In this region the properties of many atoms are still unknown, and for the present this can only be hypothetically correlated with the fact that the abundance before these atoms, which had fallen in the groups, does not change on passing to Cd^{106}_{48} and increases considerably on passing to Sn^{112}_{50}. Another offshoot of the diagonal portion of the zone is formed by Ge^{77}_{32} and Ge^{76}_{32}, the first of which has a longer half-life period than Se^{81}_{34}, while the stability of the second causes a peak in the upper boundary of the stable atoms of the 12th group. The isotopes of zirconium located to the right of Zr^{90}_{40} evidently form a horizontal offshoot of the zone. Mention has already been made of the atoms of Zr^{90}_{40}, Zr^{91}_{40} and Zr^{92}_{40} belonging to the diagonal portion of the zone in question. The stability of the atom of Zr^{96}_{40} gives rise to the peak in the upper boundary of the stable atoms of the 16th group; also corresponding to it is the second maximum of the curve of abundance of the atoms of this group. In the case of Zr^{95}_{40} and $Zr^{(97)}_{40}$ the half-life period is longer than that of Mo^{99}_{42} and Mo^{101}_{42}. Zr^{94}_{40} is the predominating atom of the group. $Zr^{(99)}_{40}$ has a long half life period and below it in the table is the predominating atom of the group.

In the left hand band of the table appears the diagonal portion of this zone, encompassing the atoms with the same values of Z + N as in the right-hand strip of the table, and the horizontal offshoot in the series of yttrium (Z = 39) and niobium (Z = 41), similar to the offshoot observed in the zirconium series (Z = 40) of the right hand band of the table. The diagonal portion of this zone passes through the following atoms located in the table in the direction from Tc^{93}_{43} to Br^{84}_{35}:

Atom	Tc^{93}_{43}	Tc^{94}_{43}	Tc^{95}_{43}	Nb^{90}_{41}	$Nb^{(91)}_{41}$	Y^{88}_{39}	Y^{89}_{39}	$Rb^{(94)}_{37}$	Rb^{87}_{37}	Br^{84}_{35}
Z + N	50	51	52	49	50	49	50	49	50	49

In the case of Tc^{93}_{43} the half-life period is only a little shorter than that of the lighter Rb^{81}_{37}. In the 8th group in the same direction are found Nb^{90}_{41}, with a half-life period exceeding that of Rb^{82}_{37}, and Tc^{94}_{43} whose half-life period is even shorter than that of Nb^{90}_{41} but is comparable with that of the lighter β^+-radioactive atoms of the same group. In the 9th group this zone embraces $Nb^{(91)}_{41}$ and Tc^{95}_{43} whose half-life period is longer than that of Y^{87}_{39}. Later on in this direction we find the stable isotopes of yttrium Y^{89}_{39} and Y^{88}_{39} whose half-life period is longer than that of the atoms occurring in the same group immediately above and below them. In the rubidium series this diagonal portion of the zone

passes through the atoms of $Rb_{37}^{(96)}$ and Rb_{37}^{97} whose half-life periods are longer than those of Y_{39}^{90} and Y_{39}^{91} respectively; it then passes through Br_{35}^{84}, the half-life of which is longer than that of Rb_{37}^{88}. Here the horizontal offshoot of this zone implies that in the case of the β^--radioactive atoms of niobium and yttrium, present in the 14th to 17th groups, and in the case of Nb_{41}^{94} the half-lives are longer than those of the heavier β^--radioactive isotopes of technetium in the respective groups.

Similar to the zones described above is the zone of stabilization indicated by the third peak in the upper (N = 24, 26, 28) and by the trough (facing the peak in the direction of the broken curve of Fig. 1) in the lower (N = 20, 24, 26) boundary of the stable atoms of the even groups of the band of even Z, resulting from the stability of the atoms of Sn_{50}^{124}, Te_{52}^{130}, Xe_{54}^{134}, Xe_{54}^{136}, Sm_{62}^{144}, Dy_{66}^{156} and Er_{68}^{162}, which in the absence of this zone of stabilization would have been radioactive. The diagonal part of this zone runs from Sm_{62}^{144} (N = 20) to Xe_{54}^{136} and encompasses the following atoms:

Atom	Sm_{62}^{144}	$Sm_{62}^{(145)}$	Nd_{60}^{142}	Nd_{60}^{143}	Ce_{58}^{140}	Ba_{56}^{137}	Ba_{56}^{138}	Xe_{54}^{135}	Xe_{54}^{136}	Te_{52}^{133}	$Te_{52}^{(134)}$
Z + N	82	83	82	83	82	81	82	81	82	81	82

The actual upper boundary of the range of stable atoms of the 28th group is Nd_{60}^{148}, lying on the previously mentioned hyperbola, passing also through Zr_{40}^{94}. Passing upward from it are atoms which are already β^--radioactive, and the stability of Xe_{54}^{134} is an anomaly due to its presence in a zone of relative stability. A similar anomaly, caused by the same zone, is the stability of Sm_{62}^{144}. The actual lower boundary of the stable atoms of the 20th group is Ce_{58}^{136}, below which is the radioactive atom of Nd_{60}^{140}. In the other groups this diagonal portion of the zone has the following features: In the case of the radioactive atoms of the lower series of the lower series of the 21st group, at first from Ba_{56}^{139} to Nd_{60}^{141}, the half-life is shortened, while on reaching Sm_{62}^{145}, (in the diagonal portion of the zone) it becomes longer. In the 22nd group the diagonal portion of the zone contains Nd_{60}^{142}, the most abundant atom of the series and (after Sn_{50}^{122}) of the group. In the 23rd group below Ba_{56}^{135} is a radioactive atom followed by the stable atom of Nd_{60}^{143}, the most abundant species of the group, and by Sm_{62}^{147}, the first of which is in the diagonal portion of the zone. Among the atoms of the 24th group on the diagonal portion of the zone is Ce_{58}^{140}, the predominating species of the pleiad to which also corresponds the second maximum of the curve of relative abundance of the atoms of this group. In the 25th group the diagonal portion of the zone passes through the atom of Ba_{56}^{137}, resulting in the stability of this atom which upsets the uniformity of the set of β^--radioactive atoms of this group. Later in the 26th group in the same direction are found Ba_{56}^{138} and Xe_{54}^{134}. Ba_{56}^{138} is the predominating species of the group and series, and the stability of Xe_{54}^{134} and of the adjacent Te_{52}^{130} (resulting from the zone of stabilization) is marked by a peak in the upper boundary of the stable atoms of this group. In the case of the β^--radioactive atoms of the 27th group from Sm_{62}^{151} to Ba_{56}^{139} the half-life is shorter in accordance with the general rule, while on transition to Xe_{54}^{135}, which is along the diagonal portion of the zone, it becomes longer. Evidently the diagonal portion of this zone extends beyond Xe_{54}^{136}, encompassing for example Te_{52}^{133} and $Te_{52}^{(134)}$, but in this region the properties of many atoms have scarcely been studied. The described diagonal portion of the zone of stabilization under consideration has two, more clearly visible offshoots, similar to those indicated for the preceeding zone. The first offshoot is formed by atoms of Sm_{62}^{147}, directly bordering on the diagonal portion of the zone, and of Dy_{66}^{156} and Er_{68}^{162}, whose stability is associated with a peak in the lower boundary of the stable atoms of the 24th and 26th groups of the band of even Z. Although there are many empty spaces in this region of the table and some of the atoms have not been reliably identified, this offshoot of the stabilization zone may also be accepted on the basis of other data. Thus, the abundance, which had fallen in the 24th and 26th groups before the atoms of Dy_{66}^{156} and Er_{68}^{162}, remains substantially unchanged on passing to the offshoot, while in the 23rd group on passing from Nd_{60}^{143} to Sm_{62}^{147} it changes slightly. In the 25th group on transition from Gd_{64}^{159} to $Dy_{66}^{(157)}$ the half-life is substantially unchanged. From the general form of this portion of the stabilization zone in the table and, in particular, from the form of the peak induced by it in the lower boundary of the stable atoms of the even groups of the band of even Z (Fig. 1), we may postulate that it will encompass also the stable or long-lived, still unknown, atoms of Sm_{62}^{146}, and Gd_{64}^{150}. The other branch of the described diagonal portion of the zone under consideration is formed by atoms of Te_{52}^{130}, the most abundant isotope of tellurium, and Sn_{50}^{124}, the predominant atom of this group, the stability of both of which results in a peak in the upper boundary of the stable atoms of the 26th and 24th group. The indicated course of the described stabilization zone accords well with the change in position of the predominating isotopes of the pleiads in this region of the table. On going from tin to tellurium they are sharply displaced to the right, into the stabilization zone, and subsequently to the left, following precisely the direction of the diagonal portion of the zone in the series of barium, cerium and neodymium. On the basis of the course of displacement in the table of the predominating isotopes of the elements from palladium to neodymium, we may postulate that the most abundant isotopes of cosmic xenon are the heavier atoms located nearer to the indicated direction of the diagonal portion of the stabilization zone than the atoms predominating in this pleiad according to the modern data [9] indicated in the table.

The diagonal portion of this zone is also clearly marked in the band of odd Z where it passes through the following atoms with the same values of Z + N, arranged in the direction from $Pm_{61}^{(143)}$ to Sb_{51}^{133}:

Atom	$Pm_{61}^{(143)}$	Pr_{59}^{141}	La_{57}^{139}	La_{57}^{139}	La_{57}^{140}	Cs_{55}^{135}	Cs_{55}^{136}	Cs_{55}^{137}	$I_{53}^{(134)}$	I_{53}^{135}	I_{53}^{136}	$Sb_{51}^{(132)}$	Sb_{51}^{133}	$Sb_{51}^{(134)}$
Z + N	82	82	81	82	83	80	81	82	81	82	83	81	82	83

The half-life of $Pm_{61}^{(143)}$ is longer than that of the lighter radioactive atoms of the 21st group which precede it and in whose case, at the start, in conformity with the general law, the half-life becomes shorter on passing from $Cs_{55}^{(131)}$ to La_{57}^{135}. In the 23rd group in the same direction we find the stable atom of Pr_{59}^{141}, which would have been radioactive in the absence of a zone of stabilization; it is below the radioactive atom of La_{57}^{137}. In the lanthanum series this zone results in the appearance of the stable isotopes La_{57}^{138} and La_{57}^{139}, which in the absence of this zone would have been β^--radioactive; the zone also results in the half-life of La_{57}^{140} being longer than that of Pr_{59}^{144}. This zone later passes through Cs_{55}^{136} and Cs_{55}^{137}, whose half-lives are longer than those of La_{57}^{140} and La_{57}^{141} respectively, then through Cs_{55}^{135}, whose half-life is very long and longer than that of the heavier β^--radioactive atoms of the same group. Subsequently the zone encompasses $I_{53}^{(134)}$, I_{53}^{135} and I_{53}^{136} in the iodine series and $Sb_{51}^{(132)}$, Sb_{51}^{133} and $Sb_{51}^{(134)}$ in the antimony series. The half-lives of which are longer than those of the atoms in the same group but below them.

Although the fourth peak in the upper (N = 36) and the oppositely located trough in the lower (N = 32) boundary of the stable atoms of the even groups of the band of even Z are quite small in comparison with the preceding three peaks, they obviously also imply a zone of stabilization since other data point to this conclusion. The diagonal portion of this zone evidently runs from Os_{76}^{184} and Os_{76}^{186} to Hf_{72}^{182}, encompassing the following atoms with Z + N from 108 to 110:

Atom	Os_{76}^{184}	Os_{76}^{186}	W_{74}^{182}	W_{74}^{183}	W_{74}^{184}	Hf_{72}^{180}	Hf_{72}^{181}
Z + N	108	109	108	109	110	108	109

The stability of Os_{76}^{184} gives rise to the peak in the lower boundary of the stable atoms of the 32nd group. On passing from W_{74}^{181} to Os_{76}^{186} the half-life period becomes slightly shorter. Further on, in the tungsten series in the same direction of this zone are found the isotopes W_{74}^{182}, W_{74}^{183} and W_{74}^{184}. They are the predominating atoms of the 34th, 35th and 36th groups respectively, and W_{74}^{184} is also the most abundant isotope of the pleiad. In the hafnium series on the diagonal portion of this zone are found Hf_{72}^{180}, Hf_{72}^{181} and Hf_{72}^{182}. Hf_{72}^{180} is the predominant isotope of the pleiad. The half-life of Hf_{72}^{181} is only very slightly shorter than that of W_{74}^{185}. Hf_{72}^{182} is still unknown but, judging by its presence in this direction and from the properties of the known atoms closest to it, it must be long-lived or even stable. Yb_{70}^{178}, whose stability results in the small convexity of the upper boundary of the stable atoms of the 36th group, is probably already present on the offshoot of this diagonal portion.

In the left-hand band of the table in this region are still many empty places and incompletely indentified atoms.

All the above noted deviations from the law of continuity of runs of single-type (stable or radioactive) atoms in the groups of the table and the great majority of deviations from the law of monotonicity of change of the half-life period of radioactive atoms in the groups of the table are caused by these zones. In the right-hand band of the table are only four deviations from the law of monotonicity, caused by the pairs $C_6^{10}-O_8^{(14)}$, $Ge_{32}^{71}-Se_{34}^{75}$, $Ba_{56}^{(140)}-Xe_{54}^{138}$ and $Er_{68}^{(165)}-Yb_{70}^{(169)}$, which are, as it were, not encompassed by these zones. It is impossible at present to draw any final conclusions about them since three of the pairs contain incompletely identified atoms, and two of the pairs approach closely to offshoots of the described zones of stabilization. This is also true of the deviations in the left-hand band of the table where there are more of them.

The described zones are similar among themselves. They all consist of diagonal portions (whose direction is indicated by the broken line in Fig. 1) with offshoots. The diagonal portions of the zones are parallel and are expressed by the general equation Z + N ≈ const. The mean value of const. for the zones in question are 28, 50, 82 and 110, which agree with the known critical ("magical") numbers found from experiment or predicted by theory. They are consequently numbers that specify the atoms present on the diagonal portions of the zones of stabilization in the system of atoms. We see from the description of the zones that these numbers are not strictly simple digits but mean values of Z + N for atoms encompassed by the diagonal portions of the zones of stabilization.

A noteworthy feature is the connection between the zones of stabilization characterizing periodicity in the

system of atoms and the periodicity in D. I. Mendeleev's system. Thus the diagonal portion of the described zones of stabilization abut at the inner edge of the right-hand band of the table onto the atoms of the eighth group of Mendeleev's periodic system: Ni, Ru, (Sm), Os, while at the outer edge of the same band they abut onto the atoms of the elements of its zero group: Ar, Kr, Xe, encompassing the atoms of elements, present in this direction, of the even series of the large periods of D. I. Mendeleev's table.

Judging by the direction of the offshoots from the diagonal portions of the described zones, we can assume that these zones are connected with one another (the 1st with the 2nd atoms of nickel, and the 2nd with the 3rd atoms of tin, the Z of which are respectively 28 and 50 in accord with the critical numbers); they are possibly only parts of a single zone of stabilization.

SUMMARY

All the known stable and radioactive atoms are arranged in a table consisting of two bands, the right-hand one containing atoms with even and the left-hand one atoms with odd nuclear charge. These two bands are divided into groups and series. This table brings out the regularities of the system of atoms more fully than the known diagrams with similar coordinates on which atoms with even and odd nuclear charge are not segregated.

Apart from the similarity, a feature is the asymmetry of distribution of the stable and radioactive atoms in the bands of the table. In the right-hand band the stable atoms form a dense field, while in the left-hand band small groups of stable atoms and singletons are separated by radioactive species. In the right-hand band in each even group the upper boundary of the stable atoms is higher and the lower boundary is lower than in the neighbouring odd groups. The converse is found in the left-hand band. The same is observed also in the change from group to group of the boundaries of the β^--radioactive atoms, of the abundance of stable atoms, and of the mass defects of atomic nuclei. The previously published diagram does not bring out these regularities.

The boundaries of the field of the stable atoms in the right-hand band contain well defined peaks and troughs caused by the zones of stabilization in the system of atoms.

In the groups of the table the stable β^--and β^+-radioactive atoms are not interspersed, as is the case in the above noted diagram, but form single-type portions of the middle, upper and lower series of the groups respectively.

In the majority of groups the half life falls monotonically, while the energy of the emitted particles monotonically increases: in the case of the β^--radioactive atoms the change is from bottom to top; in the case of the β^+--radioactive atoms it is from top to bottom. In some groups these changes are satisfactorily formulated by simple expressions.

The total mass defect of the atomic nucleus within the groups depends approximately linearly on the charge of the nucleus. On this basis, group empirical equations were obtained for calculation of the masses of atoms, which are represented approximately by parallel and equidistant straight lines and therefore are reduced to more general equations.

Atoms whose properties deviate from the described general laws of the groups and series of the table form zones of stabilization in the system of atoms. The paper describes four zones of stabilization which give rise to peaks in the upper and troughs in the lower boundary of the stable atoms of the even groups of the right-hand band of the table. They all consist of diagonal portions with offshoots by which they are possibly connected to one another. The diagonal portions of the zones are parallel and are represented by the general equation $Z + N \approx$ const. The mean value of const. for these zones is given by the numbers 28, 50, 82 and 110, in agreement with the known critical ("magical") numbers which, consequently, are not strictly whole digits.

Three of the zones described are responsible for all the exceptions to the law of continuity of runs of single-type (stable or radioactive) atoms in the groups of the table and for most of the deviations from the law of monotonic change in the groups of the table of the half-life period of the radioactive atoms and of the energy of the particles emitted by them.

A link is noted between the zones of stabilization, characterizing the periodicity in the system of atoms, and the periodicity in D. I. Mendeleev's system. The diagonal portions of the described zones of stabilization abut at the inner edge of the right-hand band onto the atoms of the 8th group of D. I. Mendeleev's table: Ni, Ru, (Sm), Os, while

at the outer edge they abut onto the atoms of its zero group: Ar, Kr, Xe, encompassing the atoms of elements of the even series of the long periods of D.I. Mendeleev's table.

LITERATURE CITED

[1] W. Heisenberg. The Physics of the Atomic Nucleus. Moscow-Leningrad, State Chemical Press 62, 170 (1947); "Scientific and Technical Bases of Nuclear Energy". Symposium edted by K. Goodman, Foreign Lit. Press 6 (1948) (Fig. 1); R. Ritsler, "Introduction to Nuclear Physics." IL, 219 (1948) and the colored table; I. Selinov in the book by Ya. I. Frenkel, Principles of the Theory of Atomic Nuceli. Moscow-Leningrad, Acad. Sci. USSR, Press, 273 (1950), Diagrams of Atomic Nuclei; I. P. Selinov, Atomic Nuclei and Nuclear Transformations. Moscow-Leningrad, State Technical Press 1 (1951) (see Tables III and IV).

[2] W. D. Harkins, J. Am. Chem. Soc., 45,1426 (1923).

[3] G. Oddo, Z. anorg. Chem., 87, 266 (1914); W. D. Harkins and E. D. Wilson, J. Am. Chem. Soc., 37, 1367, 1383 (1915); W. D. Harkins, Z. Physik, 50, 106 (1928); S. A. Shchukarev, J. Russ. Phys. Chem. Soc., Chem. Sect., 55, 447 (1924); New Ideas in Chemistry, edited by N. S. Kurnakova and S. A. Shchukarev, Symposium No. 9: "Isotopes," 61 (1924); J. Gen. Chem., 19, 3, 373, 380, 391 (1949).

[4] G. Beck, Z. Physik., 47, 407 (1928); H. L. Johnston, J. Am. Chem. Soc., 53, 2866 (1931); E. S. Sarkisov, J. Phys. Chem. USSR, 25, 1415 (1951).

[5] L. A. Chugaev, The Periodic System of the Chemical Elements. St. Petersburg, Educational Press 48 (1913); S. A. Shchukarev in the Symposium on New Ideas in Chemistry, p. 83.

[6] D. I. Mendeleev, Principles of Chemistry, 11th edition, Moscow-Leningrad, State Chemical Press, II, 302 (1932).

[7] E. Rutherford, J. Chem. Soc., 1934,635; Prog. Chem., 3, 841 (1934); Trans. Jubilee Mendeleev Congress, Moscow-Leningrad, Acad. Sci. USSR Press, 341 (1937).

[8] B. M. Kedrov in Symposium on The Periodic Law of D. I. Mendeleev and its Philosophical Significance. United State Press, Inst. Philosophy Acad. Sci. USSR, 174, 180 (1947).

[9] B. Dzhelepov and S. Petrovich, Prog. Phys. Sci., 60, 497 (1950).

[10] H. Brown, Rev. Modern Physics, 21, 625 (1949).

[11] V. I. Spitsyn in Symposium on Modern Problems of Physical Chemistry and Chemical Technology, Moscow, published by All-Union Mendeleev Chemical Society, No. 2 (1938).

[12] Scientific and Technical Principles of Nuclear Power. Symposium edited by K. Goodman. For. Lit. Press 334 (1948); G. Friedlander and J. W. Kennedy. Introduction to Radiochemistry, N.-Y., 299 (1949).

[13] G. P. Maitak, J. Exper. Theoret. Phys., 27, 39 (1954).

Received June 1, 1953

D. I. MENDELEEV'S CALCULATION OF THE RADII OF THE ATOMS

N. E. Zaev

In the fifth edition of his "Principles of Chemistry", issued in 1889, D. I. Mendeleev [1] wrote: "... the fraction A/S expresses only the mean volume corresponding to the sphere of the atoms, and therefore .... is the mean distance between the centers of the atoms", where A is the atomic weight and S is the density of the element.

D. I. Mendeleev here postulates a spherical shape for the atom.

With the availability of accurately determined Avogadro number and packing of identical spheres coefficients, it is now possible to carry out a calculation of the radii of atoms by Mendeleev's method, and to compare the results with those obtained experimentally by various methods (X-ray and electron diffraction, spectroscopy).

The literature [2-8] contains a considerable number of values of radii of atoms determined experimentally.

The following formula was used for calculation of the radius of an atom:

$$r = \sqrt[3]{\frac{3V}{4N\pi}} \cdot K,$$

where K is the packing coefficient, equal [6] for closest packing (A1 and A3) to 0.7405, for cubic space-centered packing A2 to 0,6802, for simple cubic packing to 0.5236, for tetrahedral packing (diamond, A4) to 0.3400; N = $= 6.022 \cdot 10^{23}$ molc^{-1}.

The densities of the elements and the atomic weights are mainly taken from the 1951 compilation [9]. Results of the calculations are arranged in a table with the elements listed in the order of the Russian alphabet.

The table contains four possible radii of atoms corresponding to the four most widely adopted packing coefficients.

Those values of radii are underlined in the table which can be accepted on the basis of packing data or radii known from other sources.

When evaluating the agreement between the calculated and experimental radii, we must take into account the character of the experimental method.

As we know, spectroscopic data for diatomic molecules are usually obtained to an accuracy of 0.01 A. The error is of the same order when applying the electron diffraction method to gaseous molecules.

X-ray values for crystals are more accurate when the radius is determined directly by measurements of the unit cell (as in diamond); the values obtained, however, frequently depend upon supplementary parameters which are determined from intensity data. Consequently the accuracy of X-ray values in many cases cannot be considered better than 0.1 A.

Due to the lack of data for density and packing, it was impossible to carry out calculations for the following fourteen atoms: Gd, Ac, Am, At, Cm, Np, Pu, Po, Pm, Pa, Fr, Tc, Bk, Cf.

If we take as a criterion of satisfactory agreement an absolute difference of not more than 0.01 A between the experimental and calculated values, then we see from the table that satisfactory agreement is obtained for 60 elements: Al, Ar, Be (since the packing cannot be denser than A1 or A3, the experimental data

cited by Ormont [3] appear highly improbable – r = 1.292 A and r = 1.229 A), B (it undoubtedly has diamond packing), W, Hf, Ge, Ga, Ho, Dy, Eu, Fe, In, Fr, Yb, K, Ca, Co, Si, Kr, Xe, La, Li, Lu, Mg, Mn, Cu, Mo, as (A4 packing can be assumed), Na, Nd, Ne, Ni. Nb, Sn, Os, Pd, Pt, Ra, Re, Rn, Rh, Ru, Pb, Ag, Sr, Tl, Ta, Tb, Tu, C, Ce, Zr, Er, N, H, O, F, Cl.

Assuming a satisfactory accuracy of calculation for an absolute difference between the experimental and calculated radii of much less than 0.1 A, we can add the following 14 elements to the 58 enumerated above: Ba, V, Bi, Au, Pr, Hg, Rb, Sc, Te, Ti, Th, U, Cs, Zn. If we adhere to the original criterion of comparability for these 14 elements, it is necessary to make a choice between the experimental and the calculated values of the radius.

We shall assume that the atomic weights of the elements are trustworthy. We must then postulate the existence of some errors in the experimental values of the radii or in those calculated, due to inaccurate density values.

Calculation did not give satisfactory results for 10 elements: He, P, S, Se, Br, Y, Cd, Sb, I, Sm.

As we see from the table the calculated radius of the Be atom is 0.0217 A greater than the experimental value. According to modern data [9] the density of Ba is 3.5. If the experimental radius is considered correct, then the density of Ba should be 3.6257.

The calculated radius of the V atom on the assumption of A2 packing is 1.3283 A, while the experimentally determined radius is 1.3137 A. If we accept the latter value of the radius, then the density of V is not 5.866 [9], but 6.0611.

For an atomic radius of 1.439 A for Au the density should be not 19.2 [9] but 19.433; correspondingly the density of Ir should be not 22.42 [9] but 22.816, that of Y not 5.51 [9] but 4.4993, that of Pr not 6.5 [9] but 6.8188; for Cs it remains to assume that at – 173.1° its density is 1.9932 (at 20° 1.90).

The packing coefficients for Bi, Hg, Te and U are not known. The experimental radii of atoms of Zn, Cs, Ti, and Cr show poor agreement.

The density of Sc is known roughly [9], so that it is difficult to compare the calculated and experimental radii. The assumption of closest packing made by Ormont [3] must, however, be questioned: simple cubic packing corresponds most closely to the experimental radius.

According to widely accepted data [9], the density of Ne is 1.0. At this density the experimental values of the radius agree with the caluclated values, but with different packings. According to other data [7] the density of Ne is 1.46. On accepting this density for calculation, we have satisfactory agreement between the experimental and calculated radii and the packing.

A similar discrepancy occurs with Kr.

According to the 1951 data [9] the density of Kr is 2. Other sources [10] give a density of 3.19. The latter value is more reliable, for with a density of 2 the calculated radii for all packings are remote from the experimental values. At a density of 3.19 there is complete agreement between the radius and the packing.

It is difficult to accept Ormont's statement [3] that E u has A2 packing unless we throw doubt upon the value of its density; closest packing is more probable.

On the basis of the data in [3] (no other are available) the density of Gd in our calculation will be close to 7.9792.

For Sm [3] A2 packing is indicated; according to our calculation the atomic radius may be close to 1.7445 A. For Tc, A3 packing and an inter-atomic distance of 2.735 A are cited. On this basis our calculation gives a density of 11.367 for Tc.

The calculation of interatomic distances for H, N, F, Cl and O using any available packing coefficient was found to be entirely unsuitable. The radii of these elements in the table were obtained under certain assumptions which were justified by the fact that these elements usually exist in the molecular form.

The first calculation is carried out for closest packing and therefore gives the radius of the aggregate.

Comparison of Calculated and Experimentally Determined Values of the Radii of Elements

Atomic number of element	Symbol	Calculated radius (Å) with packing				Radius (in Å) and packing according to			
		A1—A3	A2	Simple cubic	A4	Syrkin [4]	Pauling [6]	Kondratev [2]	Ormont [3]
89	Ac	—	—	—	—	—	—	—	—
13	Al	1.4311	1.3911	1.2746	1.0872	*A1*; 1.43	*A1*; 1.429	—	*A1*; 1.4289
95	Am	—	—	—	—	—	—	—	—
18	Ar	1.9227	1.8691	1.7131	1.4834	*A1*; 1.915	—	1.46	*A1*; 1.915 (40°K)
85	At	—	—	—	—	—	—	—	—
56	Ba	2.2415	2.1957	2.0123	1.7425	*A2*; 2.17	*A2*; 2.17	—	*A2*; 2.17
4	Be	1.1267	1.1037	1.0084	0.8759	*A3*; 1.11, 1.135	*A3*; 1.12, 1.134	—	*A3*; 1.13, 1.229, 1.292
97	Bk	—	—	—	—	—	—	—	—
5	B	1.030	0.9997	0.9893	0.8700	—B 0.9 ± 0.02	—	—B 0.88, = B 0.76, ≡ B 0.68	—
35	Br	1.8975	1.8446	1.6905	1.4638	1.135, 1.65	—	—Br 1.14	*A14*; 1.135
23	V	1.3663	1.3283	1.2172	1.1381	*A2*; 1.3	*A2*; 1.314	—	*A2*; 1.3157
83	Bi	1.8428	1.7918	1.7732	1.4220	1.505, 1.73	—	—	—
74	W	1.4092	1.3699	1.2554	1.0871	*A2*; 1.365	*A2*; 1.367 *A15*; 1.408	—	β-W *A15*; 1.26, 1.408
64	Gd	—	—	—	—	—	—	—	*A3*; 1.794
31	Ga	1.5476	1.4701	1.3472	1.1666	1.22, 1.3505	1.53, 1.48	—	*A11*; 1.217
72	Hf	1.5866	1.5424	1.4135	1.2240	*A3*; 1.507, 1.505	*A3*; 1.564, 1.6	—	*A3*; 1.66, 1.59
2	He	2.1062	2.0473	1.8764	1.6249	—	—	—	*A3*; 1.785
32	Ge	1.5856	1.5401	1.4115	1.2223	1.22	*A4*; 1.2225	—Ge 1.22	*A4*; 1.223
67	Ho	1.7680	1.7186	1.5751	1.3639	—	—	—	*A3*; 1.759

Continued

Atomic number of element	Symbol	Calculated radius (Å) with packing:				Radius (in Å) and packing according to:			
		A1—A3	A2	simple cubic	A4	Syrkin [4]	Pauling [6]	Kondratev [2]	Ormont [3]
66	Dy	1.7767	1.7271	1.5827	1.3707	—	—	—	A3; 1.769
63	Eu	2.0338	1.9618	1.8119	1.5690	—	—	—	A2; 2.042
26	Fe	1.2777	1.2421	1.1384	0.9850	A1; 1.26 A2; 1.24	A1; 1.26 A2; 1.239	—	A1; 1.29 (γ-Fe) A2; 1.2389 (α-Fe)
79	Au	1.4534	1.4117	1.2948	1.1212	A1; 1.44	A1; 1.439	—	A1; 1.439
49	In	1.6650	1.6186	1.4833	1.2845	1.62, 1.685	A3; 1.621, 1.685	—	A6; 1.62
53	I	1.8176	1.7668	1.6193	1.4022	1.35, 1.77	—	— I 1.33 = I 1.23	A14; 1.35
77	Ir	1.3624	1.3244	1.2138	1.0511	A1; 1.355	A1; 1.3545	—	A1; 1.3545
70	Yb	1.9396	1.8853	1.7279	1.4963	—	—	—	A1; 1.933
39	Y	1.6797	1.6328	1.4964	1.2958	A3; 1.8, 1.83	A3; 1.7975, 1.8315	—	A3; 1.81, 1.797
48	Cd	1.5632	1.5203	1.3927	1.2061	A3; 1.485, 1.645	A3; 1.4865, 1.6435	—	A3
19	K	2.3182	2.3059	2.1133	1.8441	A2; 2.31	A2; 2.309	1.9505	A2; 2.27(−175.1°C), 2.25(20° C)
98	Cf	—	—	—	—	—	—	—	—
20	Ca	1.9654	1.8960	1.7510	1.5163	A1; 1.965 A3; 1.97, 1.98	A1; 1.966 A3; 1.97, 1.9775	—	A1; 1.96 α-Ca
27	Co	1.2481	1.2133	1.1120	0.96082	A1; 1.25	A1; 1.2503 A3; 1.2495, 1.25035	—	A1; β-Co 1.253
14	Si	1.5097	1.4664	1.3440	1.1640	A4; 1.17	—	1.17	A4; 1.173
36	Kr*	1.975	1.919	1.7595	1.5237	A1; 1.97	—	—	A1; 1.975 (−252.5° C)
36	Kr**	2.3076	2.2432	2.0559	1.7803	—	—	—	—

* The specific gravity of Kr according to [10] is taken.
** The specific gravity of Kr according to [9] is taken.

Atomic number of element	Symbol	Calculated radius (Å) with packing:				Radius (in Å) and packing according to:			
		A1–A3	A2	simple cubic	A4	Syrkin [4]	Pauling [6]	Kondratev [2]	Ormont [3]
54	Xe	2.3102	2.2458	2.0583	1.7824	—	—	—	A1; 2.2 (—185.1° C)
96	Cm	—	—	—	—	—	—	—	—
57	La	1.8778	1.8267	1.6742	1.4497	—	A3; 1.8635 A1; 1.877	—	A3; α-La 1.87, 1.86
3	Li	1.5627	1.5190	1.3922	1.2056	A2; 1.502	A2; 1.502	1.335	A1; 1.559 (—196°C) A2; 1.5, 1.52 (—175.1°C)
71	Lu	1.7419	1.5936	1.5518	1.3438	—	—	—	A3; 1.737
12	Mg	1.5888	1.5563	1.4264	1.2346	A3; 1.595	A3; 1.595, 1.6015	—	A3; 1.598
25	Mn	1.3085	1.2731	1.1657	1.0093	—	A6; 1.291 1.3345	—	A1; 1.2754 α-Mn A12; 1.247 β-Mn A13; 1.265 γ-Mn A6; 1.33, 1.29
29	Cu	1.2789	1.2432	1.1393	0.9866	A1; 1.275	A1; 1.27505	—	A1; 1.2754
42	Mo	1.4022	1.3630	1.2492	1.0817	—	A2; 1.36	—	A2; 1.36
33	As	1.5660	1.5223	1.3952	1.2082	1.2505, 1.5075	1.21	—As; 1.21	—
11	Na	1.9094	1.8561	1.7011	1.4528	A2; 1.86	A2; 1.86	1.5035	1.83(—173.1°C) A2; 1.86
60	Nd	1.8308	1.7797	1.6311	1.4124	—	1.81 A3; 1.8285	—	—
10	Ne*	1.8096	1.7590	1.6122	1.3961	A1; 1.6	—	1.175	A1; 1.6
	Ne**	1.5952	1.5507	1.4212	1.2306	—	—	—	—
93	Np	—	—	—	—	—	—	—	—
28	Ni	1.2454	1.2107	1.1096	0.9608	A1; 1.245 A3; 1.245	A1; 1.2435 A3; 1.245	—	A1; β-Ni 1.2439 A3; α-Ni 1.325
41	Nb	1.4821	1.4395	1.3194	1.1424	A2; 1.425	A2; 1.4265	—	A2; 1.4264

* At d = 1.
** At d = 1.46.

Continued

Atomic number of element	Symbol	Calculated radius (Å) with packing:				Radius (in Å) and packing according to:			
		A1–A3	A2	simple cubic	A4	Syrkin [4]	Pauling [6]	Kondratev [2]	Ormont [3]
50	Sn	1.6853	1.6382	1.5014	1.3002	A4; 1.40, 1.501, 1.507	A4; 1.40 A5; 1.508, 1.588	—	A4; α-Sn 1.4
76	Os	1.3544	1.3166	1.2066	1.0449	A3; 1.335, 1.365	A3; 1.335, 1.365	—	A3; 1.364
46	Pd	1.3781	1.3397	1.2278	1.0632	A1; 1.37	A1; 1.3725	—	A1; 1.3724
78	Pt	1.3875	1.3400	1.2363	1.0706	A1; 1.385	A1; 1.3845	—	A1; 1.3845
94	P	—	—	—	—	—	—	—	—
84	Po	—	—	—	—	—	—	—	—
59	Pr	1.8539	1.8022	1.6517	1.4302	—	1.819 A3; 1.8285	—	α-Pr A3; 1.824
61	Pm	—	—	—	—	—	—	—	A2
91	Pa	—	—	—	—	—	—	—	—
88	Ra	2.3678	2.3017	2.1094	1.8267	—	—	—	—
86	Rn	2.5353	2.4644	2.2425	1.9560	—	—	—	—
75	Re	1.3757	1.3374	1.2257	1.0614	A3; 1.365, 1.38	A3; 1.3675, 1.3775	—	A3; 1.3775
45	Rh	1.3319	1.2947	1.1865	1.0275	A1; 1.34	A1; 1.342	—	β-Rh A1; 1.342
80	Hg	1.6071	1.5623	1.4318	1.2399	1.50, 1.73	1.499 A10; 1.7315	—	A10; 1.500 (—46°C)
37	Rb	2.5398	2.4689	2.2627	1.9594	A2; 2.435	A2; 2.435	—	A2; 2.43 (—173.1°C)
44	Ru	1.3473	1.3097	1.2003	0.99267	1.32 A3; 1.35	A3; 1.3225, 1.3495	—	A3; 1.348
62	Sm	1.7905	1.7445	1.5952	1.3814	—	—	—	A2; —
82	Pb	1.7504	1.7016	1.5595	1.3504	A1; 1.745	A1; 1.746	—	A1; —

Atomic number of element	Symbol	Calculated radius (Å) with packing:				Radius (in Å) and packing according to:			
		A1–A3	*A2*	simple cubic	*A4*	Syrkin [4]	Pauling [6]	Kondratev [2]	Ormont [3]
34	Se	1.6902	1.6430	1.5058	1.3040	1.16, 1.73	—	β-Se—Se $d_a = 2.1$ Å; $r = 1.17$	*A8*; $d_a = 2.32$ Å
16	S	1.6569	1.6080	1.4761	1.2782	S 1.05, 1.65	—	—S 1.04 =S 0.94 ≡S 0.87	*A16*
47	Ag	1.4494	1.4089	1.2913	1.1182	*A1*; 1.44	*A1*; 1.442	—	*A1*; 1.4417
21	Sc	1.7432	1.6945	1.5530	1.3449	—	—	—	β-Sc *A1*; 1.602
38	Sr	2.1470	2.0870	1.9127	1.6563	*A1*; 2.15	*A1*; 2.148	—	*A1*; 2.14(—173.1°C), 2.177 (room temperature)
51	Sb	1.7818	1.7188	1.5873	1.3746	1.45, 1.68	—	—	—
81	Tl	1.7173	1.6694	1.5299	1.3248	*A1*; 1.71 1.7 *A3*; 1.705	*A1*; 1.7115 1.702 *A3*; 1.725	—	*A1*; 1.711
73	Ta	1.4726	1.4319	1.3123	1.1363	*A2*; 1.425	*A2*; 1.427	—	1.4272 *A2*; 1.428
52	Te	1.8177	1.7669	1.6193	1.4026	1.43, 1.73	—	1.43, 1.37	*A8*; 1.43
65	Tb	1.7801	1.7305	1.5859	1.3733	—	—	—	*A3*; 1.773
43	Tc	—	—	—	—	—	—	—	*A3*; $\frac{d}{2} = 1.3675$
22	Ti	1.4621	1.4213	1.3026	1.1279	*A3*; 1.4505, 1.475	*A3*; 1.4507, 1.4765	—	1.438 β-Ti *A2*; (900°C)
90	Th	1.8257	1.7747	1.6265	1.4085	*A1*; 1.795	*A1*; 1.795	—	*A1*; 1.795, 1.80
69	Tu	1.7493	1.7005	1.5584	1.3495	—	—	—	*A3*; 1.742
6	C	1.001	0.90168	0.89232	0.77268	*A4*; 0.77	—	—C 0.77; 0.771 =C 0.69; 0.665 ≡C 0.61; 0.602	*A4*; 0.771

Continued

Atomic number of element	Symbol	Calculated radius (Å) with packing:				Radius (in Å) and packing according to:			
		A1–*A3*	*A2*	simple cubic	*A4*	Syrkin [4]	Pauling [6]	Kondratev [2]	Ormont [3]
92	U	1.5592	1.5087	1.3827	1.1973	*A2* 1.485	*A2*; 1.485 α-1.375 1.42 1.625 1.67	—	β-U *A2*; 1.485 α-U — all the data refuted or doubtful
15	P (red)	1.6063	1.5603	1.4299	1.2382	1.10, 1.935	—	1.1	—
87	Fr	—	—	—	—	—	—	—	—
24	Cr	1.3018	1.2654	1.1598	1.0043	*A2*; 1.245 *A3*; 1.355	*A2*; 1.246 *A3*; 1.309 *A12*	—	*A2*; α-Cr 1.2465 *A3*; β-Cr 1.35 *A12*; γ-Cr 1.222
55	Cs	2.7387	2.6621	2.4398	2.1128	*A2*; 2.62	*A2*; 2.62	—	*A2*; 2.62 (—173.1°C)
58	Ce	1.8143	1.7637	1.6164	1.3997	—	*A1*; 1.819 *A2*; 1.815	—	*A3*; α-Ce; 1.81
30	Zn	1.3905	1.3517	1.2388	1.0728	1.33 *A3*; 1.455	1.330 *A3*; 1.453	—	*A3*
40	Zr	1.6115	1.5665	1.4357	1.2432	*A2*; 1.57 *A3*; 1.61	*A2*; 1.57 *A3*; 1.583 1.611	—	α-Zr; *A3*; 1.60 β-Zr; *A2*; 1.56(842°C)
68	Er	1.7506	1.7017	1.5596	1.3505	—	—	—	*A3*; 1.748
7	N(*m*)	1.5886	—	—	—	0.545 ≡ N_2	—	= N = 0.63 ≡ N = 0.53	Cubic lattice 0.525, 0.530 at 20°K
7	$N_m^{(8)}$	0.71860	0.69855	0.63384	0.55440	—	—	—	—
1	H_m	—	—	—	—	0.37 ≡ H_2	0.37 ≡ H_2	0.31; ≡ H_2—0.374	*A3*
1	$H_m^{(54)}$	0.36566	0.35546	0.32253	0.2821	—	—	—	—
8	O_m	—	—	—	—	—	—	— O; 0.66 = O; 0.59 ≡ O; 0.52	*A1*; γ-O
8	$O_m^{(8)}$	0.6732	0.65432	0.5937	0.51928	—	—	—	—
9	F_m	1.6251	1.5797	—	1.2527	—	—	— F 0.64 = F 0.54	—
9	$F_m^{(8)}$	0.73509	0.71460	0.64840	0.56711	—	—	—	—
17	Cl_m	—	—	—	—	0.995, 1.395	—	— Cl 0.99 = Cl 0.89	0.905
17	$Cl_m^{(4)}$	1.0048	0.9782	0.88634	0.77523	—	—	—	—

Then, on the assumption that this aggregate contains n atoms in A1/ A3, A2, simple cubic and A4 packings, the radii of these atoms are found. From the table we see that the first value is obtained for elements in the atomic state. The second for atoms with single bonds, the third for atoms with double bonds, and the fourth for atoms with triple bonds. The radius r_x is calculated from the formula:

$$r_x = r_a \cdot \sqrt[3]{\frac{K}{n}} \text{ A},$$

where r_a is the radius of the aggregate.

For O, N, and F, n = 8; for Cl, n = 4; for H, n = 64. The physical meaning of these assumptions is that the atom is displaced from the center of its sphere of action along the radius of the sphere to its "external" surface.

We obtain the radius of the sphere of action of the atom as the radius of the aggregate in the first calculation. Then, introducing a whole number, we move the center of the atom by a distance of $\frac{r_a}{\sqrt[3]{n}}$ from the "external" surface of the sphere.

It is noteworthy that the radii of bonded atoms are changed in proportion to the cubic root of the packing coefficient. If l_1 is the length of a single bond, l_2 that of a double bond, and so on, and l_0 is the radius of the atom in the dissociated state (for example $N_8 \rightarrow 8N$, $F_8 \rightarrow 8F$, $Cl_4 \rightarrow 4Cl$, and so on), then

$$\frac{l_0}{l_1} = \frac{\sqrt[3]{0.7405}}{\sqrt[3]{0.6802}} = 1.0287, \quad \frac{l_1}{l_2} = \frac{\sqrt[3]{0.6802}}{\sqrt[3]{0.5236}} = 1.0918, \quad \frac{l_2}{l_3} = \frac{\sqrt[3]{0.5236}}{\sqrt[3]{0.340}} = 1.1548.$$

On this basis we can show that Cl in a triple bond will have a radius of 0.77523, while F does not give a triple bond.

Moreover, considering that the whole number n taken for calculation of the atoms in an aggregate for N, F and Cl agrees with their already known forms as N_8, F_8 and Cl_4, we may postulate the existence of hydrogen in the form of H_{64} under conditions as yet unknown.

SUMMARY

1. The atomic radii have been calculated by a refinement of the method proposed by D. I. Mendeleev. A satisfactory result was got for 60 elements and a less satisfactory result for 14 elements. An unsatisfactory result was obtained for 10 elements out of the 98. Lack of basic data prevented calculation of the atomic radii of 14 elements.

2. Evidence was obtained that in the cases of Ba, V, Au, Ir, Y, Pr and Cs, the radius of the atom and the density of the element have not been accurately determined. It was also established that the density of Ne is 1.46 and that Kr – 3.19.

3. On the basis of the data of [3], calculations gave the density of Gd (7.9792), the radius of Sm (1.7445 A) and the density of Tc (11.367).

4. It was shown that the bond length (one half of the interatomic distance) in the single and multiple bond is proportional to the cube root of the theoretical coefficient of packing of spheres of uniform diameter.

LITERATURE CITED

[1] D. I. Mendeleev, Selected Works, II. Leningrad, State Chem. Press (1934).

[2] V. N. Kondratev, The Structure of Atoms and Molecules. Moscow-Leningrad, Acad. Sci. USSR Press, (1946).

[3] B. F. Ormont, Structures of Inorganic Substances. Moscow-Leningrad, State Technical Press. (1950).

[4] Ya. K. Syrkin and M. E. Dyatkina, The Chemical Bond and the Structure of Molecules. Moscow-Leningrad, State Chemical Publishing House (1946).

[5] M. V. Volkenshtein, M. A. Elyashevich and B. M. Stepanov, Molecular Vibrations, 1–2. Moscow-Leningrad, State Technical Press (1949).

[6] L. Pauling, Nature of the Chemical Bond. Moscow-Leningrad, State Chemical Press. (1947).

[7] O. K. Rice, Electronic Structure and the Chemical Bond in Inorganic Chemistry. Foreign Lit. Press (1949).

[8] W. Hume-Rothery, Electrons and Metals. Moscow, Metallurgical Press (1949).

[9] Handbook of Chemistry, 2. Leningrad-Moscow, State Chemical Publishing House (1951).

[10] V. A. Kireev, Course of Physical Chemistry. Moscow-Leningrad, State Chemical Publishing House (1952).

Received July 14, 1954

K. E. Voroshilov Institute of Scientific
Research for Organic Intermediates and Dyes

THE SOLUBILITY PRODUCT OF HYDROXIDES OF SOME RARE ELEMENTS

L. M. Kozmin

The literature contains data for the solubility product of only a few hydroxides of rare elements, and some of the values are questionable.

Our calculations are based upon the following equation:

$$[Me^{+n}]\,[OH^-]^n = S^n \qquad (1)$$

which by substitution of $[OH^-]$ by a value can be represented in the following form:

$$\frac{[Me^{+n}]\,[1^-]^n}{[H^+]^n}\,\frac{[n]^n}{[n]^n}\,S^n = S^n \qquad (2)$$

From this we find that:

$$[H^+] = \frac{[n]}{[n]}\,\frac{[Me^{+n}]^{\frac{1}{n}}}{S} \qquad (3)$$

According to Equation (2), we can find the concentration of hydrogen ion at which a given amount concentration of Me^{+n} ion starts to come down in the form of hydroxide.

We apply Equation (3) to calculation of the hydrogen ion concentration at which $Tl(OH)_3$ starts to come down from an 0.01 M solution of a salt of thallium oxide. According to the data of Ref. No. [Illegible] and [Illegible], Thananaev [1013], the solubility product of $Tl(OH)_3$ is $1.46 \cdot 10^{-44}$. Introducing this value into Equation (3), we get:

$$[H^+] = 10^{-44}\left(\frac{0.01}{1.46 \cdot 10^{-44}}\right)^{\frac{1}{3}} = 181 \text{ g-ion/liter}$$

For a 10^{-3} M solution of $TlCl_3$ we find by this method that precipitation of $Tl(OH)_3$ starts when the hydrogen ion concentration is approximately 407 g-ion/liter. In other words, we can prepare a 10^{-3} M solution of $TlCl_3$ only on condition that the solution simultaneously also contains no less than 407 g-ion hydrogen per liter. It is unnecessary that such concentrations are unrealistic and cannot be reached. An employment of a value of the stability product of $Tl(OH)_3$ of $1.46 \cdot 10^{-44}$ leads us to grossly inaccurate results, from which we can infer that a value of the order of 10^{-44} is incorrect.

Other sources [4] give for the stability product of $Tl(OH)_3$ a value of the quite different order of 10^{-46}, which is in closer accord with the actually observed phenomena. Applying this equation (3) we get for a 10^{-3} M solution of $TlCl_3$: $[H^+] = 10^{-46}\left(\frac{0.01}{10^{-46}}\right)^{\frac{1}{3}} = 1$ g-ion/liter.

Such a hydrogen ion concentration is realistic.

Similar considerations can be applied to $Pr(OH)_3$, whose stability product was determined as 10^{-26} by J. M. Kolthoff [4]. Putting this value in equation (3) we find for a 10^{-3} M solution of salt of Pr:

$$[H^+] = 10^{-26}\left(\frac{0.01}{10^{-26}}\right)^{\frac{1}{3}} = 316 \text{ g-ion/liter}$$

i.e. once again we obtain grossly inaccurate results. For the same reason very low solubility products are found for $Th(OH)_4$, $Au(OH)_3$, SnO(OH), and other hydroxides [4].

These calculations show that the solubility products of some hydroxides require considerable correction.

In the available literature and in the handbooks we do not find values of the solubility products of the hydroxides of many rare elements. Such data are of both theoretical and practical interest. Certain data permit us to calculate the solubility product of these hydroxides. We have in mind the literature data on the pH of solutions in the instant of precipitation of the hydroxides of some rare elements from solutions of their salts of known concentration [5,6]. As was shown in one of our papers [7], these data are adequate for calculation of the solubility product.

As an example of the calculation of the solubility product, we give the calculation for frequently encountered hydroxides of the type of $Me(OH)_3$:

$$[Me^{\cdot\cdot\cdot}][OH^{-}]^3 = SP$$

$$\frac{[Me^{\cdot\cdot\cdot}]\, I^3_{H_2O}}{[H^{+}]^3} = SP \qquad (4)$$

where SP is the solubility product of the hydroxide, $[Me^{\cdot\cdot\cdot}]$ is the concentration of the cation in solution (g-ion/liter) at the start of precipitation of the hydroxide, $[H^{+}]$ is the hydrogen ion concentration at the same instant, I_{H_2O} is the ionic product of water, i.e. $10^{-14.12}$ at 18°.

Putting equation (4) into logarithmic form: $-\log [Me^{\cdot\cdot\cdot}] + 3 \log I_{H_2O} - 3 \log [H^{+}] = \log SP$,

from which:

$$3pI_{H_2O} - 3pH - \log [Me^{\cdot\cdot\cdot}] = pSP$$

At room temperature:

$$42.39 - 3pH - \log [Me^{\cdot\cdot\cdot}] = pSP \qquad (5)$$

For hydroxides of the type of $Me(OH)_4$ we obtain correspondingly:

$$56.52 - 4pH - \log [Me^{\cdot\cdot\cdot\cdot}] = pSP \qquad (6)$$

In the table are set forth the salt concentrations and the pH at the start of precipitation of the hydroxides (from the published data [5, 6]) and our values of solubility products calculated from formulas (5) and (6) for the respective hydroxides.

Solubility products of hydroxides of some rare elements

Salt	Salt concentration (M)	pH of start of precipitation at 18°	Solubility product of hydroxide
$La(NO_3)_3$ [5]	0.0133	8.35	$6.0 \cdot 10^{-20}$
$LaCl_3$ [6]	0.01	8.03	$5.0 \cdot 10^{-21}$
$La_2(SO_4)_3$ [6]	0.01	7.61	$5.5 \cdot 10^{-22}$
$LaCl_3$ [5]	0.0133	7.41	$9.1 \cdot 10^{-23}$
$Ce_2(SO_4)_3$ [6]	0.01	7.07	$1.3 \cdot 10^{-23}$
$PrCl_3$ [5]	0.0114	7.05	$6.4 \cdot 10^{-24}$
$Pr_2(SO_4)_3$ [6]	0.01	6.98	$7.1 \cdot 10^{-24}$
$Nd(NO_3)_3$ [5]	0.0133	7.00	$5.4 \cdot 10^{-24}$
$NdCl_3$ [5]	0.0114	7.02	$5.2 \cdot 10^{-24}$
$NdCl_3$ [6]	0.01	7.40	$6.4 \cdot 10^{-23}$
$Nd_2(SO_4)_3$ [6]	0.01	6.73	$1.2 \cdot 10^{-24}$
$SmCl_3$ [5]	0.0121	6.88	$2.1 \cdot 10^{-24}$
YCl_3 [5]	0.0113	6.78	$1.2 \cdot 10^{-24}$
$Th(SO_4)_2$ [6]	0.01	3.91	$1.3 \cdot 10^{-43}$
$Th(SO_4)_2$ [5]	0.01	3.53	$4.0 \cdot 10^{-45}$
$Th(NO_3)_4$ [5]	0.01	3.57	$5.7 \cdot 10^{-45}$
$ThCl_4$ [5]	0.01	3.51	$3.3 \cdot 10^{-45}$
$Ce(SO_4)_2$ [6]	0.01	2.70	$1.9 \cdot 10^{-48}$
$ZrCl_4$ [5]	0.01	1.86	$8.3 \cdot 10^{-52}$

It is interesting to note that the solubility products of a given hydroxide calculated from data taken from different sources were of the same order of magnitude in the majority of cases.

SUMMARY

1. The solubility products of the hydroxides of some rare elements, calculated on the basis of data for the pH at the start of their precipitation (cited in various publications), are of the same order of magnitude for each hydroxide, the mean values at 18° being the following:

$La(OH)_3$	$5 \cdot 10^{-21}$
$Ce(OH)_3$	$5 \cdot 10^{-23}$
$Pr(OH)_3$	$7 \cdot 10^{-24}$
$Nd(OH)_3$	$5 \cdot 10^{-24}$
$Sm(OH)_3$	$2 \cdot 10^{-24}$
$Y(OH)_3$	$1 \cdot 10^{-24}$
$Th(OH)_4$	$4 \cdot 10^{-45}$
$Ce(OH)_4$	$2 \cdot 10^{-48}$
$Zr(OH)_4$	$8 \cdot 10^{-52}$

2. Lanthanum hydroxide, the strongest base among the hydroxides of the rare earth metals, is also distinguished by a higher colubility product.

3. The solubility products of $Me(OH)_4$ are very much smaller than those of $Me(OH)_3$.

LITERATURE CITED

[1] Yu. Yu. Lurye, Mathematical and Reference table for Chemists. State Chemical Press, 103-105 (1947).

[2] N. A. Tananaev, Analytical Chemistry. United Sci.-Tech. Press, 304 (1934).

[3] N. A. Tananaev, Volumetric Analysis. United Sci.-Tech. Press, 435 (1939).

[4] I. M. Kolthoff and V. A. Stenger, Volumetric Analysis, I. State Chemical Press, 323 (1950).

[5] Ch. Britton, Hydrogen Ions. United Sci.-Tech. Press, 284 (1936).

[6] I. M. Kolthoff and E. B. Sandell, Quantitative Analysis, State Chemical Press, 72 (1948).

[7] I. M. Korenman, J. Gen. Chem., 21, 10 (1951) (T.p. 9)*

Received November 17, 1954

Gorky State University

* T.p. = C.B. Translation pagination.

THE SOLUBILITY OF ANHYDROUS METANIOBATES OF THE ALKALI METALS BY THE METHOD OF LABELED ATOMS

A. V. Lapitsky, L. N. Shishkina, M. A. Pchelkina and B. A. Stepanov

Attention to the poor solubility in water of anhydrous metaniobates of sodium and potassium was drawn by Smith and Van Hagen [1] and by Quill [2]. We have already shown[3–5] that the solubility of all the anhydrous metaniobates of the alkali metals is extremely poor, and this was confirmed by our determinations of the specific electrical conductivity of their solutions saturated at 25° [6].

We set out to study the solubility of all the anhydrous metaniobates of the alkali metals at various temperatures, using the method of radioative indicators.

EXPERIMENTAL

1. Starting substances. a) Niobium pentoxide. We have already described the method of purification of niobium pentoxide [6,7]. The niobium pentoxide that we used was sufficiently pure and did not contain appreciable amounts os impurities capable of influencing the process of formation of metaniobates of the alkali metals.

b) Carbonates of the alkali metals. Carbonates of lithium, sodium and potassium were the chemically pure grades and were not further purified. We previously prepared the carbonates of rubidium and cesium from their chlorides[6].

c) Chlorides of the alkali metals. We used chemically pure grades of cholorides of alkali metals and likewise did not purify them further.

2. Preparation of anhydrous metaniobates of the alkali metals. Due to the circumstance that we had at our disposal, for investigations of solubility of metaniobates of the alkali metals, niobium-95 in a form convenient for the preparation of active niobium pentoxide, the preparation of the investigated salts was effected by fusing active niobium pentoxide with equimolar amounts of alkali metal carbonates. As flux [8] we employed sodium fluoride. The reaction went according to the equation:

$$Me_2CO_3 + Nb_2O_5 = 2MeNbO_3 + CO_2.$$

The sodium fluoride was eliminated by treating the melt with water.

When it was desired to obtain salts containing radioactive metal, we used radioactive isotopes of the alkali metals: sodium-24 (half-life 15.10 hours), potassium-42 (half-life 12.44 hours), rubidium-86 (half-life 19.5 days) and cesium-134 (half-life 2.3 years) [9]. With these we used another method of preparation: mixtures were prepared of alkali metal chloride and niobium pentoxide in the ratio of 2:1 according to the equation: $2MeCl + Nb_2O_5 + {}^1/_2\ O_2 = 2MeNbO_3 + Cl_2$. The reaction mixtures were heated to temperatures above the melting points of the alkali metal chlorides. The excess of alkali metal chloride was removed by washing with distilled water. As was shown in preliminary experiments, anhydrous metaniobates of the alkali metals are formed under these conditions; this was confirmed by chemical analysis and X-ray data.

3. Determination of solubility of anhydrous metaniobates of alkali metals. a) Preparation of standards and methods of counting. At the bottom of an aluminum dish with a diameter of 1.5 cm was placed a filter greased with petroleum jelly. Onto the greased surface was spread a uniform layer of finely pulverized salt. By deducting the weight of the dish + filter from the weight of the dish + filter + salt, the weight of the standard was found. In order to eliminate errors during determination of specific activity due to inadequate evenness of the layer of salt on the filter, the dish containing the filter, fixed in the holder of the

counting instrument, was turned through an angle of 90° after the count, after which the count was repeated. By rotating the dish through 360° and dividing the sum of four counts by four, the specific activity of the standard was obtained.

Another method of preparation of standards consisted in mixing 50-70 mg finely pulverised active salt with water and transferring the slowly settling suspension to a small dish containing a filter. After evaporation of the water, the weight of the precipitate was determined. Layers obtained by this method proved more even.

Due to the fact that niobium-95 breaks down with loss of beta-particles of low energy (0.148 meV) and with emission of gamma-quanta possessing two components with energies of 0.752 and 0.768 meV, it was necessary to use a quartz counter or a gamma-tube. We carried out measurements both with the quartz counter and the gamma-tube counter; a comparison of the results showed, however, that the introduction of corrections for autoabsorption during use of the quartz counter is pointless since the layer is sufficiently fine.

With sodium-24, potassium-42, rubidium-86 and cesium-134, which possess beta-particles and gamma-radiations with higher energies, it was possible to employ the usual beta-tubes.

b) Determination of solubility of metaniobates of lithium, sodium, potassium, rubidium and cesium. The previously described[10,11] method of study was employed. A weighed amount of the active salt of the order of 500 mg was placed in the solubility determination vessel and distilled water was poured on to it; the mixture was then stirred for a long period at the specified temperature in the thermostat. The temperature fluctuations in the thermostat were $\pm 0.1°$. The rate of saturation of the solution was checked by taking off samples at definite intervals of time.

It was established that saturation is reached after approximately 6 hours. On the assumption that equilibrium is not reached after this period, we ran an experiment with lengthy stirring at higher temperatures (50 and 100°). It was observed that disappearance of supersaturation occurs very slowly, but the final results, within the limits of error, agree with those obtained with isothermal stirring for 6 hours. On the basis of this observation we withdrew samples 6 and 8 hours after the start of stirring. Before withdrawal of the samples, the solution was kept in the thermostat without stirring for 30 minutes. The pipet with the filter base was previously twice rinsed with active solution. The withdrawn samples of solution were cloudy and therefore required prolonged centrifuging. When studying the solubility of the salts at 50 and 75° it was necessary first to heat the pipet with the filter base. The solubility at 100° was determined in the following manner: the active salt was placed in a round-bottomed flask fitted with a condenser. Stirring was effected by boiling the solution for 10 hours. Samples were withdrawn at 100° with a special pipet equipped with a heater. Centrifuging at 50, 75 and 100° was accomplished in a thermostated centrifuge.

The filters, placed in the aluminum dish, were wetted with a specified volume of saturated active solution and then dried. The procedure for determination of the activity was the same as described in the section on "preparation of standards".

The activity of the samples ranged between 400 and 750 imp./min.; the minimum error in the measurements was determined from the formula $\Delta I = \sqrt{I + b + \sqrt{I + b}}$ [12], and the relative error from the formula $\frac{\Delta I}{I} = \delta$. The background intensity usually did not exceed 40-45 imp./min. Therefore with an intensity of the specimen of 400 imp./min. the relative error was only about 0.06, and at 750 imp./min. it was 0.065.

Results of measurements are detailed in Tables 1 to 9.

It is easy to see that the data obtained with the help of radioactive indicators sodium-24 and niobium-95 are in close agreement, thus enabling us to draw conclusions about the process of solution of sodium metaniobate and about the process of breakdown of the crystal lattice of the salt on passage into solution of ions of sodium and metaniobate.

On the basis of the data the solubility product of the sodium salt at 25° can be calculated:

$$SP = [Na^+][NbO_3^-] = [5.92 \cdot 10^{-4}][5.92 \cdot 10^{-4}] = 3.23 \cdot 10^{-7}.$$

• b is background intensity.

TABLE 1

Solubility of anhydrous lithium metaniobate (indicator niobium-95)

Temperature	Solubility (mg/ 100 ml)		Solubility (moles/ l)
	found	mean value	
0°	3.2, 3.5, 3.6	3.4	$2.30 \cdot 10^{-4}$
25	4.5, 4.3, 4.0, 4.1	4.2	$2.84 \cdot 10^{-4}$
50	6.5, 6.2, 6.5	6.4	$4.33 \cdot 10^{-4}$
75	9.1, 8.8, 8.9	8.9	$6.01 \cdot 10^{-4}$
100	11.0, 10.9	10.9	$7.36 \cdot 10^{-4}$

TABLE 2

Solubility of anhydrous sodium metaniobate at various temperatures (indicator sodium-24)

Temperature	Solubility (mg/ 100 ml)			Solubility (moles/l)
	1st expt.	2nd expt.	mean value	
0°	7.35	6.87	7.11	$4.3 \cdot 10^{-4}$
25	9.88	9.64	9.76	$5.9 \cdot 10^{-4}$
50	25.59	25.81	25.70	$1.6 \cdot 10^{-3}$
75	60.46	59.83	60.15	$3.7 \cdot 10^{-3}$
100	120.90	121.10	121.00	$7.4 \cdot 10^{-3}$

TABLE 3

Solubility of anhydrous sodium metaniobate at various temperatures (indicator niobium-95)

Temper-ature	Solubility (mg/ 100 ml)			Solubility (moles/l)
	1st expt.	2nd expt.	mean value	
0°	6.99	7.14	7.07	$4.3 \cdot 10^{-4}$
25	9.72	9.58	9.65	$5.9 \cdot 10^{-4}$
50	25.91	25.73	25.82	$1.6 \cdot 10^{-3}$
75	60.21	60.32	60.27	$3.7 \cdot 10^{-3}$
100	121.30	121.30	121.50	$7.4 \cdot 10^{-3}$

TABLE 4

Solubility of anhydrous potassium metaniobate at various temperatures (indicator potassium-42)

Temper-ature	Solubility (mg/ 100 ml)			Solubility (moles/l)
	1st expt.	2nd expt.	mean value	
0°	13.28	13.40	13.34	$7.4 \cdot 10^{-4}$
25	15.68	15.48	15.58	$8.7 \cdot 10^{-4}$
50	78.19	78.40	78.29	$4.4 \cdot 10^{-3}$
75	170.90	171.35	171.35	$9.5 \cdot 10^{-3}$
100	234.30	234.92	234.61	$1.3 \cdot 10^{-2}$

TABLE 5

Solubility of anhydrous potassium metaniobate at various temperatures (indicator niobium 95)

Temper-ature	Solubility (mg/ 100 ml)			Solubility (moles/l)
	1st expt.	2nd expt.	mean value	
0°	13.32	13.44	13.38	$7.4 \cdot 10^{-4}$
25	15.40	15.60	15.50	$8.6 \cdot 10^{-4}$
50	78.24	78.34	78.29	$4.4 \cdot 10^{-3}$
75	170.88	170.78	170.83	$9.5 \cdot 10^{-3}$
100	234.10	234.20	234.15	$1.3 \cdot 10^{-2}$

TABLE 6

Solubility of anhydrous rubidium metaniobate at various temperatures (indicator rubidium 86)

Temper-ature	Solubility (mg/ 100 ml)			Solubility (moles/ l)
	1st expt.	2nd expt.	mean value	
0°	1.9	2.1	2.0	$9.0 \cdot 10^{-5}$
25	2.3	2.5	2.4	$1.1 \cdot 10^{-4}$
50	5.1	5.3	5.2	$2.3 \cdot 10^{-4}$
75	7.6	7.6	7.6	$3.4 \cdot 10^{-4}$
100	10.2	9.8	10.0	$4.4 \cdot 10^{-4}$

Investigation of the bottom phases by X-ray and spectrographic analysis revealed constancy of composition of the salts.

Similarly from the data of Tables 4 to 7 we can calculate the solubility product at 25°: potassium metaniobate has SP = $7.48 \cdot 10^{-7}$, rubidium metaniobate SP = $5.06 \cdot 10^{-8}$.

The solubility of cesium metaniobate was determined using niobium-95 (Table 8), and at 25 to 100° using cesium-134; these results likewise show that in this case the mechanisms of solution of the salts are similar, and consequently the solubility product must be $7.55 \cdot 10^{-9}$.

TABLE 7

Solubility of anhydrous rubidium metaniobate at various temperatures (indicator niobium-95)

Temperature	Solubility (mg/100 ml) 1st expt.	2nd expt.	mean value	Solubility (moles/l)
0°	1.8	2.2	2.0	$9.0 \cdot 10^{-5}$
25	2.7	2.5	2.6	$1.11 \cdot 10^{-4}$
50	5.0	4.9	5.0	$2.21 \cdot 10^{-4}$
75	7.5	7.5	7.5	$3.3 \cdot 10^{-4}$
100	10.4	10.4	10.4	$4.6 \cdot 10^{-4}$

TABLE 8

Solubility of anhydrous cesium metaniobate at various temperatures (indicator niobium-95)

Temperature	Solubility (mg/100 ml) 1st expt.	2nd expt.	mean value	Solubility (moles/l)
0°	2.35	2.45	2.40	$8.6 \cdot 10^{-5}$
25	2.45	2.45	2.45	$8.7 \cdot 10^{-5}$
50	4.34	4.11	4.23	$1.5 \cdot 10^{-4}$
75	6.31	6.13	6.22	$2.3 \cdot 10^{-4}$
100	7.65	7.82	7.74	$2.8 \cdot 10^{-4}$

TABLE 9

Solubility polytherms of metaniobates of the alkali metals

Compound	Solubility of metaniobates of the alkali metals 0°	25°	50°	75°	100°
$LiNbO_3$	$2.3 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$
$NaNbO_3$	$4.3 \cdot 10^{-4}$	$5.9 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	$7.4 \cdot 10^{-3}$
$KNbO_3$	$7.4 \cdot 10^{-4}$	$8.7 \cdot 10^{-4}$	$4.4 \cdot 10^{-3}$	$9.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$
$RbNbO_3$	$9.0 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$
$CsNbO_3$	$8.6 \cdot 10^{-5}$	$8.7 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$

On comparing the solubility of the metaniobates of the alkali metals (Fig. 9) it is easily seen that cesium metaniobate has the lowest solubility. The solubility of the other metaniobates increases in the following order: rubidium metaniobate, lithium metaniobate, sodium metaniobate and, finally, potassium metaniobate.

SUMMARY

1. The solubility of the alkali metal metaniobates was studied at 25, 50, 75, 100°.

2. It was established that the solubility of these salts is low and decreases in the following order: potassium metaniobate, sodium metaniobate, lithium metaniobate, rubidium metaniobate, cesium metaniobate.

The solubility products of all the investigated salts were calculated at 25°.

LITERATURE CITED

[1] E. Smith, W. van-Hagen, J. Am. Chem. Soc., 37, 1785 (1915).

[2] L. L. Quill, Z. allg. anorg. Ch., 208, 257 (1932).

[3] A. V. Lapitsky, J. Gen. Chem., 16, 917 (1946).

[4] A. V. Lapitsky, J. Gen. Chem., 22, 38 (1952). (T.p. 41)•

[5] A. V. Lapitsky, J. Gen. Chem., 22, 379 (1952). (T.p. 455)•

[6] M. A. Pchelkina and A. V. Lapitsky, J. Gen. Chem., 24, 1101 (1954). (T.p. 1097)•

• T.p. = C. B. Translation pagination.

[7] Vikt. I. Spitsyn and A. V. Lapitsky, J. Gen. Chem., 15, 194 (1942).

[8] P. Holmquist, Bull. geol. Inst. Univ. Upsala, 3, 181 (1897).

[9] A. N. Nesmeyanov, A. V. Lapitsky and N. P. Rudenko, Preparation of Radioactive Isotopes, State Chemical Press (1954).

[10] B. V. Volkov and A. N. Nesmeyanov, Radiochemistry, Symposium Moscow State Univ. Press, 99 (1952).

[11] Vikt. I. Spitsyn, I. A. Savich and An. N. Nesmeyanov, Radiochemistry, Symposium Moscow State Univ. Press 91 (1952).

[12] V. I. Baranov, K. B. Zaborenko and An. N. Nesmeyanov, Radiochemistry, Symposium Moscow State Univ. Press, 27 (1952).

Received February 10, 1955

Moscow State University

INVESTIGATION OF THE SOLUBILITY OF ANHYDROUS METATANTALATES OF THE ALKALI METALS

A. V. Lapitsky, B. A. Stepanov and M. A. Pchelkina

Anhydrous metatantalates of the alkali metals are poorly soluble in water and, as we have shown [1], their saturated solutions at 25° are characterized by low electrical conductivity. The absence from the literature of any data on the solubility of metatantalates of the alkali metals induced us to carry out an investigation of this aspect.

Due to the poor solubility of the salts, we resorted to the use of radioactive indicators.

EXPERIMENTAL

1. Starting substances. a) Tantalum pentoxide. The preparation of tantalum pentoxide from "tantaloniobic" residues has already been described [2]. After purification and separation, the tantalum pentoxide was sufficiently pure and contained less than 0.3% niobium pentoxide; element impurities did not exceed 0.5%.

b) Chlorides of the alkali metals. The chlorides used in this research were chemically pure grades and were not further purified.

c) Carbonates of the alkali metals. The carbonates of lithium, sodium and potassium were chemically pure grades. The carbonates of rubidium and cesium were prepared from their chlorides as previously described [1].

2. Radioactive indicators. a) Tantalum-182. We had at our disposal a small tantalum lamina containing tantalum-182. The formation of other isotopes capable of contaminating the tantalum-182 was improbable; we therefore did not purify it further.

b) Sodium-24, potassium-42, rubidium-86 and cesium-134 were at our disposal mainly in the form of chlorides. It was necessary to purify the salts from a possible impurity (phosphorus-32) even though this was present in traces. Purification was effected by reprecipitation of the salts from their saturated solutions by passing a stream of hydrogen chloride. Purification was not carried out when we had a supply of the carbonate of the active metal (sodium-24 and potassium-42).

3. Preparation of active tantalum pentoxide. Small pieces of tantalum foil were dissolved in a mixture of equal volumes of concentrated nitric and hydrofluoric acids. Starting from a known activity of the prepared solution, a solution of tantalum fluoride in hydrofluoric acid was obtained, and to this was added a fluoride solution containing labeled tantalum. Tantalum pentoxide was precipitated with ammonia; after washing on the filter with 5% ammonium nitrate solution, it was calcined in a muffle furnace at 800°.

4. Synthesis of active metatantalates of the alkali metals. Two methods were employed. a) Active tantalum pentoxide, thoroughly stirred with an equimolar amount of the carbonate of the alkali metal and with sodium fluoride (as flux), was heated for 4-6 hours at 800-850° in a crucible furnace. After cooling, the sintered product was treated with water for removal of the sodium fluoride.

b) Tantalum pentoxide was mixed with the chloride of the active alkali metal in the ratio of 1:2, i.e. corresponding to the equation: $2MeCl + Ta_2O_5 + 1/2O_2 = 2MeTaO_3 + Cl_2$. The mixture was heated 4 hours at 800°. Unreacted metallic chloride was removed by washing with distilled water.

A proportion of the prepared salts was used as standards. The latter were prepared in the following

manner. A thin layer of petroleum jelly was spread on a piece of tracing paper which was then weighed; the finely pulverized active salt was then uniformly spread over the layer of petroleum jelly and the weight of the tracing paper + salt was determined. The standard was covered with an identical piece of tracing paper which was stuck down at the edges. Measurements were performed with the usual beta-tube; for elimination of errors due to non-uniformity of the layer of standard, the latter was turned several times through an angle of 90° while in the holder. The value obtained by dividing the sum of all these measurements by the number of 90° turns was taken as the result.

We did not introduce a correction for autoabsorption since all our isotopes were characterized by high energies of beta-particles [3].

5. Determination of solubility of metatantalates of the alkali metals. A weighed quantity of about 500 mg of the salt was placed in the solubility determination cell and distilled water was poured over it. The contents of the cell were stirred in a thermostat at constant temperature until equilibrium was reached; the temperature of the thermostat was constant to ± 0.1°. Equilibrium was generally reached after about 6 hours, as was also confirmed by the slow disappearance of supersaturation. To be quite certain that equilibrium had been reached, we stirred for 12 hours at a stirrer velocity of 200 r.p.m.

The solubilities of the salts were determined at 0, 25, 50, 75 and 100°. Samples were withdrawn after the contents of the cell had been held at a given temperature for 30 minutes. It should be noted that cloudy liquids which settled with difficulty were formed in all cases; complete settlement was not effected even after more than 20-30 hours. Due to this, we decided to centrifuge the withdrawn samples while applying the necessary precautions as described previously [4, 5]. Filters were wetted with the transparent supernatant liquids; after drying, these were inserted in tracing paper envelopes and measured in the counter. Since measurements of the samples and standards were carried out simultaneously, it was unnecessary to introduce corrections for fall in activity with passage of time.

The solubilities of metatantalates of sodium, potassium, rubidium and cesium were determined not only when using tantalum-182 but also with radioactive isotopes of the respective alkali metals. The solubility of lithium metatantalate could be determined only with tantalum-182, due to the lack of a long-lived lithium isotope[3]. Solubility data for the salts are set forth in Tables 1-9.

TABLE 1

Solubility of anhydrous lithium metatantalate at various temperatures

Temperature	Solubility (mg/100 ml)			Solubility (mole/l)
	1st sample	2nd sample	Mean	
0°	1.26	1.17	1.21	$5.14 \cdot 10^{-5}$
25	2.41	2.53	2.47	$1.05 \cdot 10^{-4}$
50	5.30	5.50	5.40	$2.29 \cdot 10^{-4}$
75	9.28	8.67	8.97	$3.81 \cdot 10^{-4}$
100	11.71	12.29	12.00	$5.09 \cdot 10^{-4}$

TABLE 2

Solubility of anhydrous sodium metatantalate at various temperatures (indicator sodium-24)

Temperature	Solubility (mg/100 ml)			Solubility (mole/l)
	1st sample	2nd sample	Mean	
0°	1.17	1.19	1.18	$4.69 \cdot 10^{-5}$
25	1.39	1.35	1.37	$5.45 \cdot 10^{-5}$
50	2.78	2.69	2.73	$1.09 \cdot 10^{-4}$
75	5.49	5.49	5.49	$2.18 \cdot 10^{-4}$
100	11.03	11.07	11.05	$4.39 \cdot 10^{-4}$

The activity of the specimens was 400 to 1200 imp./min., giving a relative error of the measurements of 0.06–0.05 [3].

A comparison of the solubilities of sodium metatantalate found with the help of sodium-24 and tantalum-182 readily reveals that the process of solution is accompanied by passage into solution of equal amounts of sodium and tantalate ions. On the basis of this observation we can calculate the solubility product of sodium metatantalate:

$$SP = [Na^+][TaO_3^-] = [5.47 \cdot 10^{-5}][5.47 \cdot 10^{-5}] = 2.99 \cdot 10^{-9}.$$

On the basis of data for the solubility of potassium tantalate at 25°, $SP = 2.37 \cdot 10^{-9}$.

Taking the solubility of anhydrous rubidium metatantalate at 25° to be $3.84 \cdot 10^{-5}$ mole/l, SP = $= 1.47 \cdot 10^{-9}$.

TABLE 3

Solubility of anhydrous sodium metatantalate at various temperatures (indicator tantalum-182)

Temperature	Solubility (mg/100ml) 1st sample	2nd sample	Mean	Solubility (mole/l)
0°	1.20	1.16	1.18	$4.69 \cdot 10^{-5}$
25	1.42	1.34	1.38	$5.47 \cdot 10^{-5}$
50	2.74	2.80	2.77	$1.10 \cdot 10^{-4}$
75	5.54	5.48	5.51	$2.19 \cdot 10^{-4}$
100	10.96	11.08	11.02	$4.38 \cdot 10^{-4}$

TABLE 4

Solubility of anhydrous potassium metatantalate at various temperatures (indicator potassium-42)

Temperature	Solubility (mg/100ml) 1st sample	2nd sample	Mean	Solubility (mole/l)
0°	1.17	1.16	1.17	$4.36 \cdot 10^{-5}$
25	1.31	1.30	1.31	$4.89 \cdot 10^{-5}$
50	3.31	3.19	3.25	$1.21 \cdot 10^{-4}$
75	7.79	7.72	7.75	$2.89 \cdot 10^{-4}$
100	13.24	12.77	13.00	$4.86 \cdot 10^{-4}$

TABLE 5

Solubility of anhydrous potassium metatantalate at various temperatures (indicator tantalum-182)

Temperature	Solubility (mg/100ml) 1st sample	2nd sample	Mean	Solubility (mole/l)
0°	1.12	1.19	1.16	$4.32 \cdot 10^{-5}$
25	1.35	1.24	1.30	$4.85 \cdot 10^{-5}$
50	3.34	3.28	3.32	$1.23 \cdot 10^{-4}$
75	7.81	7.64	7.73	$2.87 \cdot 10^{-4}$
100	13.38	13.00	13.19	$4.92 \cdot 10^{-4}$

TABLE 6

Solubility of anhydrous rubidium metatantalate at various temperatures (indicator rubidium-86)

Temperature	Solubility (mg/100ml) 1st sample	2nd sample	Mean	Solubility (mole/l)
0°	0.96	0.96	0.96	$3.05 \cdot 10^{-5}$
25	1.21	1.21	1.21	$3.85 \cdot 10^{-5}$
50	2.70	2.74	2.72	$8.65 \cdot 10^{-5}$
75	6.04	6.32	6.18	$1.97 \cdot 10^{-4}$
100	8.42	8.73	8.58	$2.73 \cdot 10^{-4}$

TABLE 7

Solubility of anhydrous rubidium metatantalate at various temperatures (indicator tantalum-182)

Temperature	Solubility (mg/100ml) 1st sample	2nd sample	Mean	Solubility (mole/l)
0°	0.98	1.00	0.99	$3.06 \cdot 10^{-5}$
25	1.17	1.15	1.16	$3.83 \cdot 10^{-5}$
50	2.66	2.82	2.74	$8.66 \cdot 10^{-5}$
75	6.15	6.17	6.16	$1.96 \cdot 10^{-4}$
100	8.54	8.62	8.58	$2.73 \cdot 10^{-4}$

TABLE 8

Solubility of anhydrous cesium metatantalate at various temperatures (indicator cesium-134)

Temperature	Solubility (mg/100ml) 1st sample	2nd sample	Mean	Solubility (mole/l)
0°	1.01	1.04	1.02	$2.82 \cdot 10^{-5}$
25	1.08	1.16	1.12	$3.09 \cdot 10^{-5}$
50	1.66	1.58	1.62	$4.48 \cdot 10^{-5}$
75	4.16	4.08	4.12	$1.13 \cdot 10^{-4}$
100	4.68	4.82	4.75	$1.31 \cdot 10^{-4}$

On the basis of solubility data for cesium metatantalate at 25°, $SP = 9.49 \cdot 10^{-10}$.

As in the investigation of metaniobates of the alkali metals [5], we carried out X-ray and chemical analyses of the bottom phases and obtained confirmatory evidence of the constancy of composition of the salt.

A comparison of the solubility polytherms of the alkali metal metatantalates reveals the noteworthy fact (Table 10) that the solubility falls off in the direction from lithium tantalate to cesium tantalate.

TABLE 9

Solubility of cesium metatantalate at various temperatures (indicator tantalum-182)

Temperature	Solubility (mg/100 ml) 1st sample		Mean	Solubility (mole/l)
0°	0.98	1.02	1.00	$2.83 \cdot 10^{-5}$
25	1.10	1.12	1.11	$3.07 \cdot 10^{-5}$
50	1.60	1.66	1.63	$4.50 \cdot 10^{-5}$
75	4.16	4.04	4.10	$1.13 \cdot 10^{-4}$
100	4.74	4.76	4.75	$1.31 \cdot 10^{-4}$

TABLE 10

Polytherms of solubility of metatantalates of the alkali metals

Compound studied	Solubility (mole/l)				
	0°	25°	50°	75°	100°
$LiTaO_3$	$5.14 \cdot 10^{-5}$	$1.05 \cdot 10^{-4}$	$2.29 \cdot 10^{-4}$	$3.81 \cdot 10^{-4}$	$5.09 \cdot 10^{-4}$
$NaTaO_3$	$4.69 \cdot 10^{-5}$	$5.46 \cdot 10^{-5}$	$1.10 \cdot 10^{-4}$	$2.19 \cdot 10^{-4}$	$2.89 \cdot 10^{-4}$
$KTaO_3$	$4.34 \cdot 10^{-5}$	$4.87 \cdot 10^{-5}$	$1.22 \cdot 10^{-4}$	$2.88 \cdot 10^{-4}$	$4.89 \cdot 10^{-4}$
$RbTaO_3$	$3.06 \cdot 10^{-5}$	$3.84 \cdot 10^{-5}$	$8.66 \cdot 10^{-5}$	$1.97 \cdot 10^{-4}$	$2.73 \cdot 10^{-4}$
$CsTaO_3$	$2.83 \cdot 10^{-5}$	$3.08 \cdot 10^{-5}$	$4.49 \cdot 10^{-5}$	$1.13 \cdot 10^{-4}$	$1.31 \cdot 10^{-4}$

SUMMARY

1. The solubility polytherms of the metatantalates of the alkali metals were studied in the temperature range of 0 to 100°.

2. It was observed that the solubility of alkali metal metatantalates falls off with rising atomic weight of the element.

3. The 25° solubility data served as a basis for calculation of the solubility products of the anhydrous metatantalates of the alkali metals.

LITERATURE CITED

[1] M. A. Pchelkina and A. V. Lapitsky, J. Gen. Chem., 24, 1101 (1954). (T.p. 1097)*

[2] V. A. Pchelkin, A. F. Efimov and A. V. Lapitsky, J. Gen. Chem., 24, 1284 (1954). (T.p. 1287)*

[3] An. N. Nesmeyanov, A. V. Lapitsky and N. P. Rudenko, Preparation of Radioactive Isotopes, State Chemical Press (1954).

[4] A. V. Lapitsky and S. P. Alekhin, Factory Lab., 21, 1246 (1955).

[5] A. V. Lapitsky, M. A. Pchelkina, L. N. Shishkina and B. A. Stepanov, J. Gen. Chem., 25, 1862 (1955). (T.p. 1835)*

[6] V. I. Baranov, K. B. Zaborenko and An. N. Nesmeyanov, Radiochemistry. Moscow State University Press, 27 (1952).

Received February 10, 1955

Moscow State University

* T.p. = C. B. Translation pagination.

TERNARY SYSTEMS WITH LAYERING WITHOUT FORMATION OF CHEMICAL COMPOUNDS

I. L. Krupatkin

Among the ternary systems with equilibruim between the liquid phases, special attention is merited by those which contain two binary layered systems. This is because in those ternary systems it very often happens that the regions of layering extending from the boundaries of the binary systems inside the prism of the ternary system form in it a single surface of layering of the ternary system. This surface occupies the whole of the concentration range facing the binary homogeneous system, so that it can reflect the interaction between the components of the investigated homogeneous system throughout the whole of its concentration range.

The literature contains examples of studies of ternary systems with two binary layerings[1–4] the majority of these, however, appear to be variants of the special case in which intensive chemical interaction or even formation of chemical compounds occurs in the binary homogeneous system of the given three-component system. Inadequate study has hitherto been made of cases in which interaction is very weak and compounds are not formed in the binary homogeneous system of a given ternary system with two binary layerings. Only a few isolated examples of such systems can be found in the literature [5]. Nevertheless, it is generally assumed, when describing liquid-phase equilibria, that in ternary systems with two binary layerings without chemical interaction between the components, the layering curves approximate straight lines.

In order to check this assumption, a special study has now been made of the problem with reference to a series of ternary systems satisfying the specified conditions. These have been investigated for their layering characteristics, and the experimental equilibrium curves for the liquid phases have been evaluated.

EXPERIMENTAL

The following four three-component systems were examined in connection with the study of the forms of the liquid-phase equilibria curves: water–isoamyl alcohol–tertiary isoamyl alcohol, water–o-toluidine–aniline, glycerol–o-toluidine–diethylaniline, glycerol–furfural–benzaldehyde.

In the first two systems the water, alcohols and amines gave layering; in the second pair of systems the glycerol layered with the amines and aldehydes. Consequently, each of these ternary systems contains two binary systems which layer. Concerning the binary homogeneous systems entering into the given ternary systems, they are formed in the first ternary system with the alcohols, in the second and third systems with amines, and in the fourth system with the aldehydes; no chemical compounds are formed between the constituents of the organic compounds involved. Thus all four three-component systems selected for investigation satisfy the necessary conditions, namely that they are ternary systems with two binary layerings without formation of chemical compounds in the three binary homogeneous systems.

The investigation was conducted by the isothermal method [6] in ampoules with ground-glass stoppers in a water thermostat. Mixtures of the homogeneous binary system of the required composition were charged into an ampoule, and at a specified constant temperature they were titrated with the third component until turbidity developed. The compositions of the points of the isotherms were then calculated on the basis of the amounts of the components by weight.

The following substances were used: The alcohols were distilled and the isoamyl alcohol fraction boiling at 114° and the tertiary amyl alcohol fraction boiling at 102° were collected. The amines were also distilled and the o-toluidine fraction boiling at 200°, the aniline fraction boiling at 184° and the diethylaniline fraction boiling at 216° were collected. The water was twice distilled. The glycerol was pharmacutical grade with b. p. 290°. The aldehydes were rectified and a furfural fraction coming over at 162° and a

benzaldehyde fraction coming over at 179° were collected.

In the ternary system formed by the alcohols with water, the layering isotherms were studied from both sides of the surface of equilibrium between the liquid phases. In the remaining ternary systems the layering isotherms were studied only from one side of the surface in question due to the very poor solubility of the amines in water and glycerol, and of the aldehydes in glycerol.

Ternary system water–isoamyl alcohol–tertiary isoamyl alcohol was studied at 20 and 50°. In addition to titration with water of the pure alcohols, mixtures of the alcohols containing 10, 20, 30, 40, 50, 60, 70, 80 and 90% isoamyl alcohol were also titrated. The solubility of the alcohols and their 50% mixture in water was also investigated (Table 1 and 2, Fig. 1). The data show that at 20° the solubility of water in the two isoamyl alcohols is fairly high and nearly the same for both alcohols – of the order of 14%; isoamyl alcohol is slightly less soluble than the second alcohol. By contrast the solubility of the alcohols in water at the same temperature is considerably lower; as in the former case the solubility of isoamyl alcohol (6.20%) is a little lower than that of tertiary isoamyl alcohol (9.23%). In this system the temperature profoundly influences the reciprocal solubility of the components and their mixtures. However, this influence is not the same for both alcohols. With temperature rise from 20 to 50° the solubility of isoamyl alcohol increases to 4%, and that of tertiary isoamyl alcohol falls to 6%. Fig. 1 shows that the solubility isotherms are curves with negative deviation. This may be the consequence of dissociation in water of the associated molecules of the alcohols into simple molecules. Fig. 1 indicates that the deviation increases with rising temperature, corresponding to increasing dissociation of the associated molecules of alcohols with rising temperature.

TABLE 1

Composition of the points of the isotherms of solubility of water in isoamyl and tertiary isoamyl alcohols and their mixtures

Content (in weight-%)			Content (in weight-%)		
of water	isoamyl alcohol	tertiary isoamyl alcohol	of water	isoamyl alcohol	tertiary isoamyl alcohol
	20°			50°	
14.80	0.00	85.20	21.12	0.00	78.88
14.48	8.55	76.97	18.84	8.11	73.05
12.93	17.42	69.65	18.07	16.38	65.55
13.52	25.95	60.53	17.13	24.87	52.00
12.82	34.88	52.30	17.00	33.20	49.80
12.20	43.90	43.90	15.05	42.50	42.45
12.44	52.56	35.00	16.29	50.22	33.49
12.45	61.32	26.23	16.52	58.45	25.03
13.24	69.44	17.32	17.22	66.24	16.54
13.04	78.30	8.66	17.39	74.34	8.27
14.54	85.46	0.00	17.98	82.02	0.00

The ternary system water–o-toluidine–aniline was studied at 20 and 50°. Apart from the individual amines, titration with water was effected of their mixtures containing 10, 20, 30, 40, 50, 60, 70, 80 and 90% aniline (Table 3, Fig. 2). At 20° the solubility of water in the amines and their mixtures is low – of the order of 5-6%; that of o-toluidine is higher than that of aniline. With rise of temperature from 20 to 50° the solubility of water increases slightly to 6-8%, the increase again being slightly greater with o-toluidine than with aniline. Consequently in this system the temperature has an insignificant influence upon the mutual solubility of the components and their mixtures. It is noteworthy, as shown by Fig. 2, that in this ternary system the solubility isotherms are substantially straight lines.

TABLE 2

Composition of points of the isotherm of solubility of isoamyl and tertiary isoamyl alcohols and their mixtures in water at 20°.

Content (weight-%)		
of water	isoamyl alcohol	tertiary isoamyl alcohol
90.77	0.00	9.23
93.12	3.44	3.44
93.80	6.20	0.00

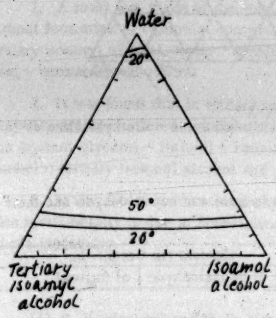


Fig. 1. Isotherms of solubility of the ternary system water – isoamyl alcohol – tertiary isoamyl alcohol at 20 and 50°.

The ternary system – glycerol – o-toluidine – diethylaniline was investigated at 18°. In this system apart from the pure amines, titration with glycerol was also effected of their mixtures containing 10, 20, 30 30, 40, 50, 60, 70, 80, and 90% diethylaniline (Table 4, Fig. 3). The data of Table 4 show that the solubilities of glycerol in diethylaniline and in o-toluidine differ markedly. In diethylaniline the solubility is not more than 1%, whereas in o-toluidine it reaches 10%. From Fig. 3. we see that the solubility isotherm of this ternary system is almost rectilinear with a small negative deviation.

The ternary system glycerol – furfural – benzaldehyde was studied at 20 and 50°. At these temperatures titrations with glycerol were carried out both on the individual aldehydes and on their mixtures containing 10, 20, 30, 40, 50, 60, 70, 80, and 90% benzaldehyde (Table 5, Fig. 4).

TABLE 3

Composition of points of the isotherms of solubility of water in aniline and o-toluidine and their mixtures

Content (weight %)			Content (weight %)		
of aniline	o-toluidine	water	of aniline	o-toluidine	water
20°			50°		
0.00	93.77	6.23	0.00	92.23	7.77
9.39	84.54	6.07	9.24	83.19	7.57
18.86	75.41	5.73	18.50	74.02	7.48
28.32	66.03	5.65	27.78	64.80	7.42
37.96	56.97	5.07	37.16	55.78	7.06
47.50	47.47	5.03	46.70	46.73	6.57
57.60	38.17	4.23	56.28	37.57	6.16
66.71	28.60	4.69	65.73	28.16	6.11
76.24	19.05	4.71	75.44	18.84	5.72
85.68	9.54	4.78	84.69	9.43	5.88
95.00	0.00	5.00	93.85	0.00	6.15

TABLE 4

Composition of points of the isotherm of solubility of glycerol in o-toluidine and diethylaniline and their mixtures at 18°

Content (weight %)		
of diethyl-aniline	of o-toluid-ine	of glycer-ol
0.00	89.94	10.06
9.22	82.98	7.80
18.76	75.05	6.19
28.35	66.15	5.50
37.82	56.74	5.44
47.72	47.72	4.56
57.83	38.55	3.62
68.15	29.20	2.65
78.62	19.66	1.72
88.52	9.84	1.64
98.96	0.00	1.04

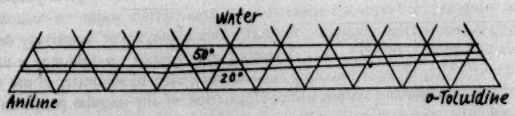


Fig. 2. Isotherms of solubility of the ternary system water – o-toluidine – aniline at 20 and 50°.

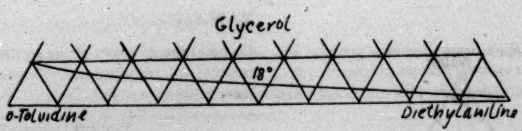


Fig. 3. Isotherm of solubility of the ternary system glycerol – o-toluidine – diethylaniline at 18°.

TABLE 5

Compositions of points of the isotherms of solubility of glycerol in furfural and benzaldehyde and their mixtures

Content (in weight-%)			Content (in weight-%)		
of glycerol	of benzaldehyde	of furfural	of glycerol	of benzaldehyde	of furfural
	20°			50°	
6.20	0.00	93.80	6.60	0.00	93.40
4.60	9.54	85.86	5.40	9.46	85.14
4.80	19.04	76.16	5.70	18.86	75.44
5.60	28.32	66.08	7.40	27.78	64.82
6.50	37.40	56.10	8.10	36.76	55.14
6.20	46.90	46.90	8.60	45.70	45.70
6.70	55.98	37.32	8.90	54.66	36.44
6.60	65.38	28.02	9.40	63.42	27.18
6.90	74.48	18.62	9.40	72.48	18.12
6.50	84.15	9.35	9.00	81.90	9.10
6.10	93.90	0.00	6.90	93.10	0.00

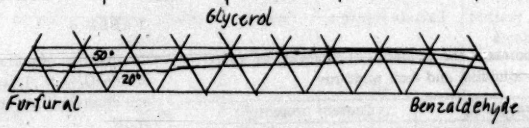


Fig. 4. Solubility isotherms of the ternary system glycerol – furfural – benzaldehyde at 20 and 50°.

Table 5 shows that the solubility of glycerol in both aldehydes (and their mixtures) at 20° are very similar and of the order of 6%. With rise of temperature to 50° the solubility of glycerol in the individual aldehydes increases to a very slight extent – not more than several tenths of a percent. In mixtures, however, especially those with a high benzaldehyde content, rising temperature is accompanied by a marked rise in solubility to a figure of 9.4%. Consequently, in this system the temperature influences not so much the solubility of glycerol in the individual aldehydes as the solubility in their mixtures. Fig. 4 shows that the isotherms of solubility in this ternary system are curves with a slight positive deviation which becomes more marked at higher temperatures.

From the foregoing experimental material we can draw conclusions about the character of the isotherms of equilibrium between the liquid phases in ternary systems with two binary layerings without formation of chemical compounds in the binary homogeneous systems entering into the ternary systems. In ternary systems of this type three forms of isothermal curves without any singular points are actually encountered. These solubility isotherms are either straight lines (system water – o-toluidine – aniline) or positively deviating curves (system glycerol – furfural – benzaldehyde) or negatively deviating curves (systems water – isoamyl alcohol – tertiary isoamyl alcohol and glycerol – o-toluidine – diethylaniline). On all these curves the solubility changes smoothly between the points of solubility of the third component in the components of the homogeneous system without formation of any singular points on the isotherms. The deviations of the solubility curves from rectilinearity are due, as explained above, to processes of association and dissociation of the components of the systems.

SUMMARY

1. A study was made of the liquid-phase equilibria in ternary systems containing two binary layerings without formation of chemical compounds in the third binary homogeneous system: water – isoamyl alcohol – tertiary isoamyl alcohol, water – o-toluidine – aniline, glycerol – o-toluidine – diethylaniline, glycerol – furfural – benzaldehyde.

2. It was found that in ternary systems of this type, the following three forms of isothermal curves of solubility are encountered: straight lines (system water – o-toluidine – aniline), curves with positive deviation (system glycerol – furfural – benzaldehyde), and curves with negative deviation (systems water – isoamyl alcohol – tertiary isoamyl alcohol and glycerol – o-toluidine – diethylaniline).

3. It was shown that in ternary systems of the indicated type the deviation of the solubility isotherms from rectilinearity is due to dissociation of the associated molecules of the components of the systems into simple molecules.

LITERATURE CITED

[1] R. V. Mertslin and V. D. Vasev, J. Gen. Chem., 21, 417 (1951). (T.p. 463)*

[2] K. I. Mochalov, J. Gen. Chem., 8, 529 (1938).

[3] E. F. Zhuravlev, J. Gen. Chem., 12, 639 (1938); 10, 22, 1926 (1940).

[4] I. L. Krupatkin, J. Gen. Chem., 22, 184 (1952); Sup. Vol. II, 771 (1953). (T.p. 229)*

[5] Meerburg, Z. phys. Chem., 40, 641 (1902).

[6] Bancroft, Phys. Revs., 3, 130 (1895).

Received October 11, 1954

Cherkass State Institute of Pedagogy

* T.p. = C. B. Translation pagination.

THE TERNARY RECIPROCAL SYSTEM OF THE FLUORIDES AND SILICATES OF LITHIUM AND CALCIUM

A. G. Bergman and N. A. Bychkova

The investigation of the reciprocal system Li, Ca | F, SiO_3 was undertaken with the objective of clarifying the possibility of the application of the visual-polythermal method to the study of silicate salt and silicate systems. Up to now silicate systems have been examined by the rather laborious methods of quenching, annealing, etc. which are not always trustworthy and unequivocal.

EXPERIMENTAL

The investigation was carried out by the visual-polythermal method of fusion. The crucible and stirrer were of platinum. A Pt – Pt/Rh thermocouple and a reflecting scale graduated in 10 mV were used. The liquidus curves were determined from the temperatures of appearance and disappearance of crystals; the interval between them was reduced to a minimum. The melting point was taken as the temperature mean between appearance and disappearance of crystals. Fusion was effected in a shaft electric furnace. The fusion temperature was up to 1150 – 1200°. The inherent radiance of the furnace and of the melt was suppressed by illumination from above with a strong light beam from a lamp of the TR-4 type.

LiF and CaF_2 were prepared from the chemically pure carbonates and twice distilled, chemically pure hydrofluoric acid, while Li_2SiO_3 was prepared by sintering and then fusion of chemically pure lithium carbonate and spectrally pure quartz sand in a Silit furnace. $CaSiO_3$ was added during the operation in the form of chemically pure CaO and SiO_2 (the latter got by calcination of silicic acid). Results are presented as equimolar percentages. Part of the experimental material has been omitted from the tables to save space.

Binary systems. 1. $Li_2SiO_3 - CaSiO_3$ (Table 1, Fig. 1). Using the method of cooling curves [1], a eutectic was found at 979° and 43.7 mole-% $CaSiO_3$; according to our data the eutectic is at 1024° and 45.5 mole-% $CaSiO_3$. The character of the reciprocal system Li, Ca|| F, SiO_3 adjacent to the $Li_2SO_3 - CaSiO_3$ side confirms the correctness of our results. Due to the high refractoriness of the components, the system was studied in the range of 25 to 57.5% $CaSiO_3$.

TABLE 1

System $Li_2SiO_3 - CaSiO_3$

$CaSiO_3$ (mole %)	Temperature	$CaSiO_3$ (mole %)	Temperature	$CaSiO_3$ (mole %)	Temperature
25	1106°	37	1060°	49	1050°
28	1094	40	1046	52	1072
31	1082	43	1034	55	1100
34	1072	46	1027	57.5	1126

2. $Li_2F_2 - Li_2SiO_3$ (Table 2, Fig. 1). Here studied for the first time;* a compound was detected, melting with decomposition, with the suggested formula $2LiF \cdot Li_2SiO_3$ (arbitrarily disignated D). The eutectic corresponds to 840° and 5% Li_2SiO_3. A polymorphic transformation of Li_2SiO_3 was detected at 986°.

3. $Li_2F_2 - CaF_2$ (Table 3, Fig. 1). Previously studied [2], repeated by us. The system has a eutectic at 769° and 33% CaF_2.

* A. G. Bergman, N. A. Bychkova and A. K. Nesterova [6].

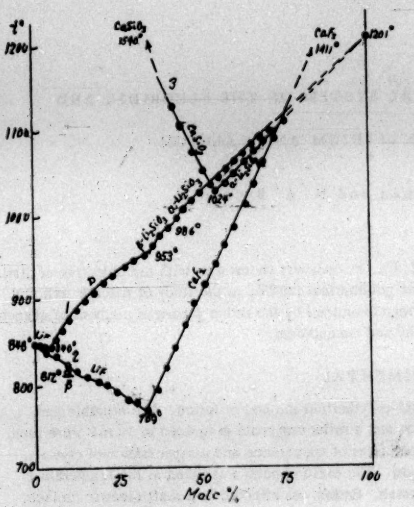


Fig. 1. Binary systems.

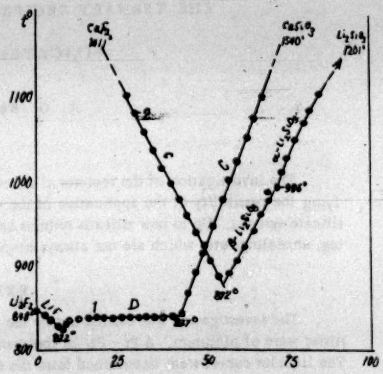


Fig. 2. Diagonal sections of the reciprocal system. 1) $Li_2F_2-CaSiO_3$, 2–$CaF_2-Li_2SiO_3$.

TABLE 2

System $Li_2F_2-Li_2SiO_3$

Li_2SiO_3 (mole%)	Temperature	Li_2SiO_3 (mole%)	Temperature	Li_2SiO_3 (mole %)	Temperature
0	848°	21	916°	48	1014°
1.5	846	24	924	50.5	1024
3	844	27	936	53	1032
4.5	842	30	945	55.5	1040
6	850	33	950	58	1050
7.5	862	35.5	960	60.5	1060
10	874	38	972	63	1070
12.5	886	40.5	982	65.5	1080
15	894	43	994	68	1088
18	906	45.5	1004	70.5	1098

TABLE 3

System $Li_2F_2-CaF_2$

CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature
0	848°	27	782°	51	916°
3	840	30	776	54	940
6	833	33	769	57	962
9	825	36	792	60	986
12	817	39	816	63	1012
15	810	42	842	66	1036
18	804	45	867	69	1062
21	796	48	895	72	1090
24	791				

TABLE 4

Diagonal of $Li_2F_2-CaSiO_3$

$CaSiO_3$ (mole%)	Temperature	$CaSiO_3$ (mole%)	Temperature	$CaSiO_3$ (mole%)	Temperature
0	848°	22.5	836°	47.5	890°
2	842	25	837	50	916
4	836	27.5	837	52.5	943
6	828	30	837	55	973
8	830	32.5	837	57.5	996
10	836	35	837	60	1018
12.5	837	37.5	837	62.5	1046
15	838	40	837	65	1070
17.5	837	42.5	840	67.5	1094
20	837	45	862	—	—

TABLE 5

Diagonal of $Li_2SiO_3-CaF_2$

CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature
15	1100°	35	942°	55	955°
17.5	1082	37.5	926	57.5	976
20	1074	40	908	60	996
22.5	1044	42	892	62.5	1016
25	1025	44	877	65	1036
27	1004	46	884	67.5	1056
29	983	48	904	70	1080
31	971	50	918	72.5	1099
33	957	52.5	937		

4. $CaF_2-CaSiO_3$. Was previously studied [3] by the thermodynamic method of plotting of cooling curves; only a eutectic at 1130° and 48 mole-% CaF_2 was detected.

We did not study this system due to its refractoriness. A study of the reciprocal system one of whose sides is the system $CaF_2-CaSiO_3$, and a comparison with other data showed that it was most probable that in the reciprocal system (Figs. 3 and 8) the field of crystallization (arbitrarily designated C) corresponds to a compound whose composition is on the $CaF_2-CaSiO_3$ side (the composition $CaF_2 \cdot 2CaSiO_3$ is proposed). The latter accords with the topological data of the reciprocal system.

Diagonal sections. Both diagonal sections of the system are unstable since they intersect the fields of the complex compounds.

1. $Li_2F_2-CaSiO_3$ (Table 4, Fig. 2) was studied up to 67,5% $CaSiO_3$. The crystallization curve intersects the field of the component LiF and the two complexes D ($2LiF \cdot Li_2SiO_3$) and C ($CaF_2 \cdot 2CaSiO_3$). The branch of complex D is horizontal, indicating the identity of the directions of the diagonal section and of the isotherms in this field. Taking into account the outline of field C and of the contiguous field of $CaSiO_3$ (Fig. 3), we must conclude that the diagonal of $Li_2F_2-CaSiO_3$ extends from field C to the field of $CaSiO_3$.

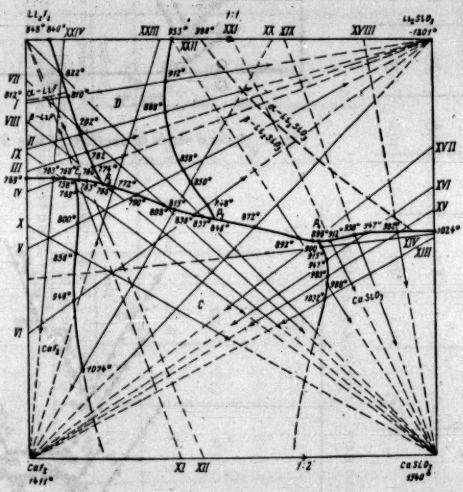


Fig. 3. Arrangements of cross-sections of system Li, Ca // F, SiO_3.

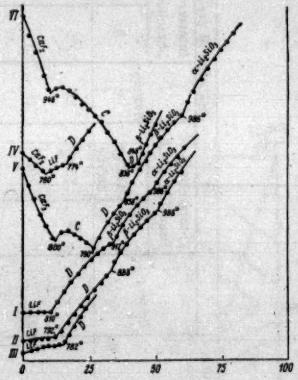


Fig. 4. First series of cross-sections (Table 6).

2. $Li_2SiO_3-CaF_2$ (Table 5,* Fig. 2). In the region examined up to 72,5% CaF_2, this section has three crystallization branches. The branches of compound C ($CaF_2 \cdot 2CaSiO_3$) and of Li_2SiO_3 intersect at 872° and 44,5% CaF_2. At 986° the branches of the α- and β-modifications of Li_2SiO_3 intersect. Judging by the form of the CaF_2/C boundary line (Fig. 3), the diagonal extends from the field of the complex C into the field of the component CaF_2.

Internal cross-sections. 24 internal cross-sections were studied (Fig. 3).

* Following Table 6, tables in this article do not appear in sequence.

TABLE 6

Cross-section number	Original composition and direction of cross-sections	Branches of crystallization curves and their intersections											
		Branch 1	Intersections of branches 1 and 2		Branch 2	Intersections of branches 2 and 3		Branch 3	Intersections of branches 3 and 4		Branch 4	Intersections of branches 4 and 5	
			A*	Temperature		A	Temperature		A	Temperature		A	Temperature
I	15% CaF_2 + 85% $(LiF)_2$ → Li_2SiO_3	LiF	10.5	810°	D	33.5	912°	β-Li_2SiO_3	48	986°	α-Li_2SiO_3 + α'-Li_2SiO_3		
II	26% CaF_2 + 74% $(LiF)_2$ → Li_2SiO_3	LiF	12	792	D	33	888	β-Li_2SiO_3	51	986			
III	31.5% CaF_2 + 68.5% $(LiF)_2$ → Li_2SiO_3	LiF	14.5	782	D								
IV	36% CaF_2 + 64% $(LiF)_2$ → Li_2SiO_3	CaF_2	8.5	760	LiF	16	774	D					
V	50% CaF_2 + 50% $(LiF)_2$ → Li_2SiO_3	CaF_2	12	800	C	26.5	790	D	38	858	β-Li_2SiO_3	61	986°**
VI	70% CaF_2 + 30% $(LiF)_2$ → Li_2SiO_3	CaF_2	10.5	946	C	40.5	836	D	44	848	β-Li_2SiO_3		

* A Percentage content of added component. ** 5th branch α-Li_2SiO_3.

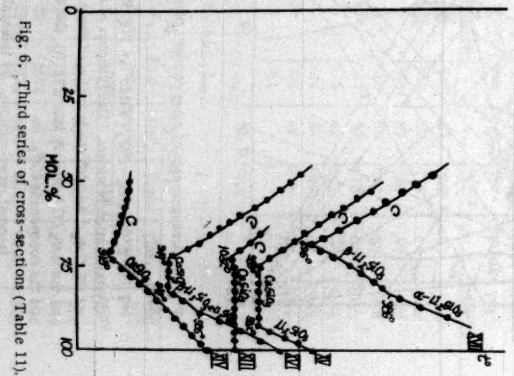


Fig. 6. Third series of cross-sections (Table 11).

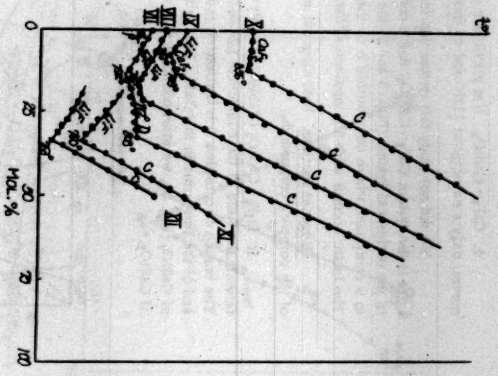


Fig. 5. Second series of sections (Table 9).

Note: Tables in this article do not follow in sequence.

TABLE 9

Cross-section number	Original composition in the direction of the cross-sections	Branches of the crystallization curves and their intersections									
		Branch 1	Intersections of branches 1 and 2		Branch 2	Intersections of branches 2 and 3		Branch 3	Intersections of branches 3 and 4		Branch 4
			A*	Temperature		A	Temperature		A	Temperature	
VII	10% CaF_2, 90% $(LiF)_2$ → $CaSiO_3$	α-LiF	4.0	812°	β-LiF	13	792°	D	32.5	808°	C
VIII	20% CaF_2, 80% $(LiF)_2$ → $CaSiO_3$	LiF	17.5	766	**	21	772	C			
IX	27.5% CaF_2, 72.5% $(LiF)_2$ → $CaSiO_3$	LiF	6.5	763	CaF_2	12	769	C			
X	45% CaF_2, 55% $(LiF)_2$ → $CaSiO_3$	CaF_2	11	856	C						
XI	37% $CaSiO_3$, 63% CaF_2 → $(LiF)_2$	C	56.5	760	LiF						
XII	42.5% $CaSiO_3$, 57.5% CaF_2 → $(LiF)_2$	C	56	763	LiF						

* A Percentage content of added component. ** Lines of common crystallization of C and D.

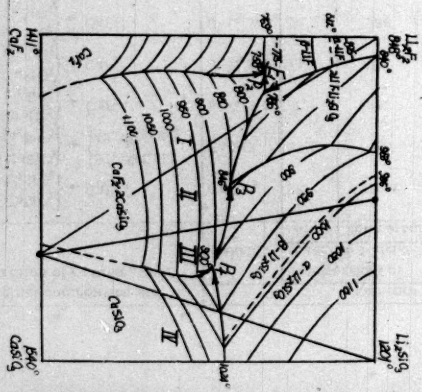


Fig. 8. Projection of the 3-dimensional diagram of the reciprocal system Li, Ca || F, SiO_3.

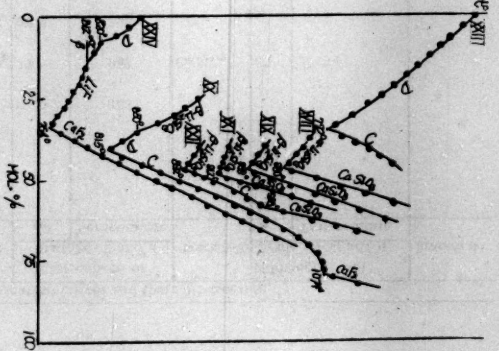


Fig. 7. Fourth series of cross-sections (Table 14).

TABLE 12

Cross-section number	Original composition and direction of cross-sections	Branches of the crystallization curves and their intersection											
		Branch 1	Intersections of branches 1 and 2		Branch 2	Intersections of branches 2 and 3		Branch 3	Intersections of branches 3 and 4		Branch 4
			A*	Temperature		A	Temperature		A	Temperature	
XIII	47% $CaSiO_3$ 53% Li_2SiO_3 → CaF_2	$CaSiO_3$	28	1032°	C						
XIV	46.5% $CaSiO_3$ 53. % Li_2SiO_3 → {57.5% CaF_2 {42.5% $(LiF)_2$	$CaSiO_3$	28.5	915	C						
XV	41% $CaSiO_3$ 59% Li_2SiO_3 → CaF_2	α - Li_2SiO_3	7.5	982	$CaSiO_3$	25.5	983°	C			
XVI	35% $CaSiO_3$ 65% Li_2SiO_3 → CaF_2	α - Li_2SiO_3	11	986	β - Li_2SiO_3	17	947	$CaSiO_3$	27	947°	C
XVII	25% $CaSiO_3$ 75% Li_2SiO_3 → CaF_2	α - Li_2SiO_3	16.5	986	β - Li_2SiO_3	30.5	896	C			

* A Percentage content of added component.

Fig. 9. Projection of the curves of common crystallization on the CaF_2–$CaSiO_3$ side.

TABLE 13

CaF_2 (mole %)	Temperature	CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature
0	1046°	15	982°	32.5	1025°
2	1030	17.5	982	35	1038
4	1015	20	982	37.5	1052
6	996	22.5	983	40	1068
8	982	25	983	42.5	1082
10	982	27.5	994	45	1100
12.5	982	30	1014	47.5	1115

The first series of cross-sections (I–VI) (Table 6, Fig. 4) permits us to delineate mainly the fields of the components LiF and CaF_2 and to fix the boundaries between the fields of Li_2SiO_3 and complex D and of complex C and complex D.

Second series of cross-sections VII–XII (Table 9, Fig. 5). With the help of this series of sections the boundaries of the LiF and CaF_2 fields and of the D and C complexes from the side of the LiF and CaF_2 fields were established.

TABLE 10

Cross-section VII

$CaSiO_3$ (mole %)	Temperature	$CaSiO_3$ (mole %)	Temperature	$CaSiO_3$ (mole %)	Temperature
0	823°	22.5	800°	47.5	938°
2.5	817	25	802	50	963
4	812	27.5	804	52.5	993
6	810	30	806	55	1016
9	803	32.5	808	57.5	1035
12.5	794	35	830	60	1057
		37.5	856	62.5	1080
15	794	40	872	65	1100
17.5	797	42.5	895		
20	798	45	916		

TABLE 11

Cross-section X

$CaSiO_3$ (mole %)	Temperature	$CaSiO_3$ (mole %)	Temperature	$CaSiO_3$ (mole %)	Temperature
0	860°	15	884°	32.5	1010°
2.5	860	17.5	904	35	1026
5	860	20	920	37.5	1045
7	860	22.5	940	40	1064
9	858	25	958	42.5	1080
11	856	27.5	974	45	1100
13	871	30	994		

TABLE 15

Cross-section XX

CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature	CaF_2 (mole%)	Temperature
25	924°	40	820°	55	945°	70	1057°
27.5	910	42.5	833	57.5	967	72.5	1066
30	895	45	858	60	987	75	1072
32.5	878	47.5	880	62.5	1006	77.5	1074
35	850	50	903	65	1026	80	1084
37.5	836	52.5	925	67.5	1046	82.5	1114

TABLE 16

Cross-section XIV

CaF_2 (mole%)	Temperature	CaF_2 (mole %)	Temperature	CaF_2 (mole %)	Temperature	CaF_2 (mole %)	Temperature
0	870°	17.5	802°	35	774°	52.5	909°
2.5	858	20	797	37.5	791	55	930
5	840	22.5	792	40	807	57.5	950
7.5	824	25	785	42.5	826	60	972
10	818	27.5	780	45	846	62.5	993
12.5	814	30	772	47.5	866	65	1012
15	807	32.5	766	50	890	67.5	1030

TABLE 17

Field number	Field	Area (in %)		Field number	Field	Area (in %)
1	LiF		3.7	5	$CaSiO_3$	16.5
2	α-Li_2SiO_3	29.6	16.4	6	$2LiF \cdot Li_2SiO_3$	9.2
3	β-Li_2SiO_3		13.2	7	$CaF_2 \cdot 2CaSiO_3$	32.2
4	CaF_2		8.8			

Projection of the 3-dimensional diagram of the recriprocal system (Fig. 8). 7 fields of crystallization were detected in the system. Of these, 5 belong to components (the Li_2SO_3 field is divided into two by the polymorphic transformation) and 2 to the side complexes: D (presumed to be $2LiF \cdot Li_2SiO_3$) and C (presumed to be $CaF_2 \cdot 2CaSiO_3$). We do not analyze the LiF field through which also passes the boundary line of the homeomorphic transformation at 812°.

TABLE 14

Cross-section number	Original composition and direction of cross-sections	Branches of crystallization curves and their intersections											
		Branch 1	Intersections of branches 1 and 2		Branch 2	Intersections of branches 2 and 3		Branch 3	Intersections of branches 3 and 4		Branch 4
			A*	Temperature		A	Temperature		A	Temperature	
XVIII	17.5% $(LiF)_2$ → $CaSiO_3$ 82.5% Li_2SiO_3	α-Li_2SiO_3	46.5	980°	$CaSiO_3$						
XIX	37.5% $(LiF)_2$ → $CaSiO_3$ 62.5% Li_2SiO_3	β-Li_2SiO_3	47	938	$CaSiO_3$						
XX	40% $(LiF)_2$ → CaF_2 60% Li_2SiO_3	β-Li_2SiO_3	35	850	D	41	815°	C	79.5	1074°	CaF_2
XXI	50% $(LiF)_2$ → $CaSiO_3$ 50% Li_2SiO_3	β-Li_2SiO_3	48.5	912	$CaSiO_3$						
XXII	65% $(LiF)_2$ → $CaSiO_3$ 35% Li_2SiO_3	β-Li_2SiO_3	46.5	892	C	58.5	988	$CaSiO_3$			
XXIII	67.5% $(LiF)_2$ → CaF_2 32.5% Li_2SiO_3	D	35	772	C						
XIV	91% $(LiF)_2$ → CaF_2 9% Li_2SiO_3	D	8	820	α-LiF	13	812	β-LiF	33.5	764	CaF_2

* A) Percentage content of added component.

TABLE 7

Cross-section I

Li_2SiO_3 (mole %)	Temperature	Li_2SiO_3 (mole%)	Temperature	Li_2SiO_3 (mole %)	Temperature
0	810°	22.5	876°	45	976°
2.5	811	25	885	47.5	984
4.5	810	27.5	894	50	1000
7.5	812	30	902	52.5	1016
10	810	32.5	908	55.5	1025
12.5	825	35	920	57.5	1037
15	840	37.5	938	60	1048
17.5	854	40	952		
20	865	42.5	965		

TABLE 8

Cross-section V

Li_2SiO_3 (mole %)	Temperature	Li_2SiO_3 (mole %)	Temperature	Li_2SiO_3 (mole %)	Temperature
0	908°	29	805°	57.5	974°
2	883	31.5	828	60	982
4	862	34	840	62.5	1003
6.5	840	36.5	852	65	1020
9	824	39	870	67.5	1036
11.5	805	41.5	885	70	1052
14	814	44	904	72.5	1065
16.5	814	46.5	916	75	1078
19	810	48.5	926	77.5	1090
21.5	804	50	936	80	1104
24	800	52.5	950		
25.5	790	55	960		

Third series of cross-sections XIII–XVII (Table 11, Fig. 6) defines the boundary lines between the fields of lithium silicate and calcium silicate and complex C.

In cross-sections XIII, XV and XVI the crystallization branches have a horizontal portion which indicates that the course of these sections coincides with the isotherms in the $CaSiO_3$ field.

Fourth series of cross-sections XVIII–XXIV (Table 14, Fig. 7). The temperature limits of all the crystallization fields of the system are accurately delineated with the help of the cross-sections of the fourth series.

The areas of the crystallization fields, expressed in percentages of the total area of the square of composition of the system, are set forth in Table 17. The projection of the points and lines onto the $CaF_2-CaSiO_3$ side is represented in Fig. 9.

The system contains two complexes. One of them, D ($2LiF \cdot Li_2SiO_3$), starts from the investigated system $Li_2F_2-Li_2SiO_3$; the other is assumed to start from the $CaF_2-CaSiO_3$ side. Analysis of the reciprocal system as a whole indicates that the complex (assumed to be $CaF_2 \cdot 2CaSiO_3$) belongs to the $CaF_2-CaSiO_3$ system. These data for the $CaF_2-CaSiO_3$ system eliminate the inconsistency between the order of crystallization of slag• as indicated by microstructural investigation on the one hand [4] and by phase data for the $CaF_2-CaSiO_3$ side on the other hand [3]. The microstructural data for the order of crystallization of slag are fully in accord with our hypothesis of the character of the $CaF_2-CaSiO_3$ system. The literature [4] contains a contradiction between microstructural data for the order of crystallization of slag and the composite system on the basis of the data for the $CaF_2-CaSiO_3$ side [3].

For this reciprocal system it was not possible to calculate the standard thermal effect of the exchange reaction due to the lack of data for the heat of formation of $CaSiO_3$. It is clear, however, that it could not have been determined in the direction of the reaction since complex formation is a conspicuous feature in the system; consequently none of the diagonals is either a stable or a triangulating secant. The triangulation scheme of the system is represented in Fig. 8. Corresponding to the triangle I is the invariant eutectic point E_1 (758°); II is marked by the transition point P_2 (766°), III by point (846°), and IV by P_4 (900°).

According to the classification of A. G. Bergman and G. A. Bukhalova [5], the system belongs to the adiagonal-belt type of reversible-reciprocal systems.

SUMMARY

1. The visual-polythermal fusion method was applied to an investigation of the liquidus surface of binary systems of the fluorides and silicates of lithium and calcium: $Li_2F_2-Li_2SiO_3$, $Li_2SiO_3-CaSiO_3$, $Li_2F_2-CaF_2$, and of the crystallization surface of the ternary reciprocal system Li, Ca F, SiO_3.

2. The crystallization surface of the reciprocal system consists of seven crystallization fields, one eutectic and three transition-invariant points.

3. The system bolongs to the adiagonal-belt typeoof reciprocal systems.

4. Investigation by the visual-polythermal method of this system and of a series of other systems involving silicate components has shown the complete possibility of study of silicate and silicate-salt systems by the simple and rapid visual-polythermal method.

LITERATURE CITED

[1] R. C. Wallace, Z. allg. anorg. Chem., 63, 1 (1909).

[2] G. A. Bukhalova and A. G. Bergman, Proc. Acad. Sci. USSR, 66, 67 (1949).

[3] B. Karandeeff, Z. allg. anorg. Chem., 68, 188 (1910).

[4] V. V. Lapin, Proc. Acad. Sci. USSR, 31, 695 (1941).

[5] A. G. Bergman and G. A. Bukhalova, J. Gen. Chem., 20, 235 (1950). (T.p. 245)••

[6] A. G. Bergman, N. A. Bychkova and A. K. Nesterova, Proc. Acad. Sci. USSR, 101, 483 (1955).

Received January 12, 1955

Rostov-on-Don State University

• Translator's note: Are welding slag is referred to in the original paper.

•• T.p. = C. B. Translation pagination.

DOUBLE DECOMPOSITION IN THE ABSENCE OF A SOLVENT

THE RECIPROCAL SYSTEM OF THE SULFATES AND METABORATES OF LITHIUM AND POTASSIUM

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

We have previously studied the system of the tungstates and metaborates of lithium and potassium Li, K || WO_4, BO_2. In the present paper we submit the results of investigation of the analogous system containing sulfate in place of tungstate with the objective of comparing two systems with components of similar character.

The standard thermal effect of the double decomposition reaction could not be calculated because the heats of formation were unknown; for the same reason it was impossible to predict the direction of the exchange reaction and the scheme of the phase diagram.

EXPERIMENTAL

Binary system. 1) $K_2SO_4-K_2(BO_2)_2$ (Table 1, Fig. 1) consists of two branches: K_2SO_4 and $K_2(BO_2)_2$, with a eutectic at 848° and 42.5% K_2SO_4. 2) $Li_2SO_4-Li_2(BO_2)_2$ (Table 1, Fig. 1); the fusion curve consists of three branches: Li_2SO_4, the compound $3Li_2SO_4 \cdot 2LiBO_2$, and $Li_2(BO_2)_2$, which interesect at 737° and 18% $Li_2(BO_2)_2$ and 737° and 31% $Li_2(BO_2)_2$. The compound $3Li_2SO_4 \cdot 2LiBO_2$ • found by us melts without decomposition at 742°. Transition of the α- and β-forms of $Li_2(BO_2)_2$ is observed at 815° and 70% $Li_2(BO_2)_2$. 3) $Li_2(BO_2)_2-K_2(BO_2)_2$ (Table 1, Fig. 1): the branches of $K_2(BO_2)_2$ and $Li_2(BO_2)_2$ intersect at 582° and 56% $Li_2(BO_2)_2$. Transition of the α- and β-forms of $Li_2(BO_2)_2$ is observed at 794° and 89% $Li_2(BO_2)_2$. 4) K_2SO_4 (Table 1, Fig. 1) was studied previously [1]; the fusion curve has five branches: α- and β-Li_2SO_4, a compound (2:1) $2Li_2SO_4 \cdot K_2SO_4$, melting with decomposition, a compound (1:1) $Li_2SO_4 \cdot K_2SO_4$ melting without decomposition and with a maximum at 732°, and K_2SO_4. The points of intersection are at 532° and 76.5% Li_2SO_4, 712° and 39.5% Li_2SO_4. Transition of the α- and β-forms of Li_2SO_4 occurs at 572° and 14% K_2SO_4.

Stable diagonal cross-section of $K_2SO_4-Li_2(BO_2)_2$. It has the character of a binary system with a eutectic turning point at 730° and 45% K_2SO_4. Transition of the α-and β-forms of $Li_2(BO_2)_2$ is noticed at 800° and 10% K_2SO_4 (Table 2, Fig. 2).

Unstable diagonal cross-section of $Li_2SO_4-K_2(BO_2)_2$. Consists of six branches of crystallization: Li_2SO_4, D_1, β-$Li_2(BO_2)_2$, D_2, K_2SO_4 and $K_2(BO_2)_2$, intersecting respectively at 640° and 7.5% $K_2(BO_2)_2$, 724° and 17.5% $K_2(BO_2)_2$, 750° and 28.5% $K_2(BO_2)_2$, 744° and 50% $K_2(BO_2)_2$, 782° and 82.5% $K_2(BO_2)_2$ (Table 2, Fig. 2).

Stable adiagonal cross-section $D_2-Li_2(BO_2)_2$ is a binary system with a eutectic turning point at 750° and 35% $Li_2(BO_2)_2$ (Table 2, Fig. 2).

Internal cross-sections. Sections at the K_2SO_4 vertex (Table 3, Fig. 3). Cross-section III: 50% $K_2(BO_2)_2$ + 50% $Li_2(BO_2)_2$: 2 branches of crystallization of $K_2(BO_2)_2$ and K_2SO_4 intersecting at 632° and 7% K_2SO_4. Cross-section X: 27.5% $K_2(BO_2)_2$ + 72.5% $Li_2(BO_2)_2$: branches β-$Li_2(BO_2)_2$ and K_2SO_4 intersect at 650° and 6.5% K_2SO_4. Cross-section XI: 32.5% $K_2(BO_2)_2$ + 67.5% $Li_2(BO_2)_2$: branches: β-$Li_2(BO_2)_2$ and K_2SO_4 intersecting at 600° and 4% K_2SO_4. Cross-section XIII: 70% $Li_2(BO_2)_2$ + 30% Li_2SO_4: branches: β-$Li_2(BO_2)_2$, D_2 and K_2SO_4 intersecting at 740° and 37% K_2SO_4; 738° and 57.5% K_2SO_4. Belt cross-section I: 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$ → → 50% Li_2SO_4 + 50% K_2SO_4 has three branches: $K_2(BO_2)_2$, K_2SO_4 and compound D_2, intersecting at 614° and 6.5% mixture (50% Li_2SO_4 + 50% K_2SO_4), 744° and 50% mixture (50% Li_2SO_4 + 50% K_2SO_4).•

• In the remainder of the paper and in the diagrams $3Li_2SO_4 \cdot 2Li_2BO_2$ is designated D_1, and $Li_2SO_4 \cdot K_2SO_4$ is designated D_2.

•• In the tables are presented only the minimum number of points necessary for plotting the fusion curves; in the diagrams they are given in full.

TABLE 1

$K_2(BO_2)_2$—K_2SO_4		Li_2SO_4—$Li_2(BO_2)_2$		Li_2SO_4—K_2SO_4		$Li_2(BO_2)_2$—$K_2(BO_2)_2$	
% K_2SO_4	t°	% $Li_2(BO_2)_2$	t°	% K_2SO_4	t°	% $Li_2(BO_2)_2$	t°
0	947	0	860	0	856	0.0	947
5	924	5	820	5	752	5.0	920
10	919	10	782	10	650	10.0	900
15	898	15	750	15	556	15.0	884
20	886	20	740	18	542	25.0	846
25	878	25	742	20	536	35.0	790
30	872	30	738	22	542	45.0	718
35	862	35	750	24	574	50.0	672
40	852	40	764	26	600	55.0	590
42.5	848	42.5	770	28	625	57.5	604
45	858	45	774	30	648	60.0	624
50	872	50	786	32	666	65.0	660
55	884	55	796	35	688	70.0	692
60	900	60	802	38	702	80.0	764
65	918	65	808	42	722	85.0	790
70	936	70	815	46	730	87.5	794
75	956	75	820	50	732	90.0	798
80	978	80	826	60	716	92.5	810
90	1000	90	836	70	825	95.0	820
100	1069	100	843	100	1069	100.0	843

TABLE 2

Stable diagonal of Li_2SO_4—$K_2(BO_2)_2$				Unstable diagonal of K_2SO_4—$Li_2(BO_2)_2$				Stable diagonal of D_2—$Li_2(BO_2)_2$	
% Li_2SO_4	t°	% Li_2SO_4	t°	% K_2SO_4	t°	% K_2SO_4	t°	% $Li_2(BO_2)_2$	t°
0	860	40	760	0	843	40	738	0	736
2.5	770	42.5	760	2.5	834	42.5	734	5	737
5	700	45	758	5.0	820	45	730	10	740
7.5	640	47.5	755	7.5	812	47.5	736	15	742
10	690	50	744	10	800	50	746	20	744
12.5	710	52.5	782	12.5	798	52.5	764	25	745
15	720	55	800	15	796	55	774	30	747
17.5	724	60	820	17.5	790	57.5	786	35	750
20	740	65	830	20	782	60	800	40	755
22.5	744	70	830	22.5	776	65	820	45	760
25	748	75	826	25	772	70	850	50	764
27.5	750	80	800	27.5	764	80	892	60	772
30	755	82.5	782	30	756	90	964	70	780
32.5	760	85	808	32.5	750	100	1069	80	792
35	762	90	860	35	750	—	—	85	800
37.5	762	100	947	37.5	746	—	—	100	843

TABLE 3

Internal cross-sections at the K_2SO_4 vertex

Cross-section III		Cross-section X		Cross-section XIII		Cross-section XIV		Cross-section I (percent of mixture (95% Li_2SO_4 + 5% K_2SO_4))		Cross-section XI	
% K_2SO_4	t°	% K_2SO_4	t°	% K_2SO_4	t°	% K_2SO_4	t°		t°	% K_2SO_4	t°
0	672	0	710	0	814	0	830	0	672	0	680
2.5	660	2.5	690	10	676	10	800	2.5	650	2.5	630
5	644	5	670	20	772	20	780	5	628	5	620
7.5	632	7.5	670	30	754	30	760	7.5	678	7.5	670
10	716	10	692	35	744	40	738	10	724	10	710
20	800	20	756	40	750	42.5	738	20	780	15	742
30	828	30	786	45	752	45	744	30	786	20	765
40	852	40	812	50	752	50	752	40	770		
50	872	50	834	55	746	55	752	50	744		
60	890	60	860	60	750	60	785	60	744		

TABLE 4

Internal sections at the Li_2SO_4 vertex

Cross-section II		Cross-section IV		Cross-section V		Cross-section VI		Cross-section VII		Cross-section VIII		Cross-section IX	
% Li_2SO_4	t°	% Li_2SO_4	t°	% Li_2SO_4	t°	% Li_2SO_4	t°	% Li_2SO_4	t°	% Li_2SO_4	t°	% Li_2SO_4	t°
0	672	0	956	0	872	0	878	0	846	0	602	0	676
2.5	640	10	934	10	885	2.5	852	5	782	2.5	594	2.5	620
5	614	20	904	20	890	5	840	10	726	5	618	5	610
7.5	684	30	846	30	856	7.5	828	12.5	738	10	706	7.5	660
10	708	35	784	40	770	10	834	15	774	12.5	718	10	700
15	740	40	738	42.5	730	20	858	20	800	15	728	12.5	698
20	750	42.5	728	45	736	30	850	30	800	20	716	15	690
25	734	45	734	47.5	738	40	802	40	738	22.5	716	17.5	710
30	716	50	738	50	740	45	760	42.5	730	25	738	20	724
35	750	60	742	55	752	50	750	45	735	30	756	30	774

TABLE 5

Internal cross-sections at the $Li_2(BO_2)_2$ and (50% Li_2SO_4 + 50% K_2SO_4) vertices

Cross-section XV		Cross-section XVI		Cross-section XVII		Cross-section XVIII		Cross-section XIX		Cross-section XX		Cross-section XXI	
				percent of mixture		percent of mixture		percent of mixture		percent of mixture		percent of mixture	
% $Li_2(BO_2)_2$	t°	% $Li_2(BO_2)_2$	t°	(50% Li_2SO_4 + 50% K_2SO_4)	t°	(50% Li_2SO_4 + 50% K_2SO_4)	t°	(50% Li_2SO_4 + 50% K_2SO_4)	t°	(50% Li_2SO_4 + 50% K_2SO_4)	t°	(50% Li_2SO_4 + 50% K_2SO_4)	t°
0	700	0	550	0	782	0	742	0	750	0	774	0	808
2.5	670	1	562	2.5	730	5	734	5	784	5	770	5	802
5	650	2	562	5	720	10	730	10	746	10	765	10	796
7.5	646	3	598	7.5	700	12.5	726	15	742	15	758	15	785
10	670	4	620	10	678	15	723	20	738	20	750	20	770
15	716	5	638	12.5	660	20	720	22.5	732	25	733	25	755
20	730	10	698	15	645	22.5	718	25	732	30	738	27.5	746
25	734	15	720	17.5	632	25	720	27.5	734	35	738	30	746
27.5	740	20	730	20	660	30	724	30	736			35	738
30	744	22.5	735	22.5	675	35	728	35	736				
35	755	25	740	25	700								

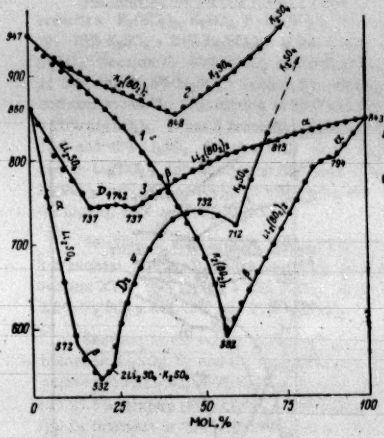


Fig. 1. Binary systems.
1) $(LiBO_2)_2(KBO_2)$, 2) $(KBO_2)_2 - K_2SO_4$, 3) $Li_2SO_4 - Li_2(BO_2)_2$, 4) $Li_2SO_4 - K_2SO_4$.

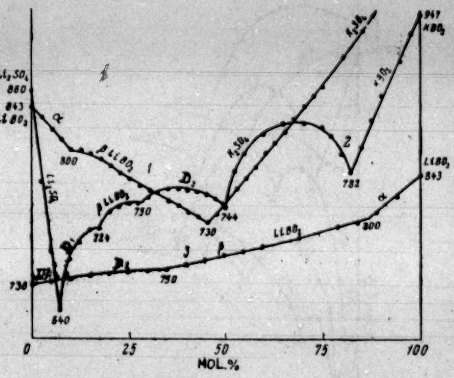


Fig. 2. Diagonal cross-sections.
1) $Li_2(BO_2)_2 - K_2SO_4$, 2) $Li_2SO_4 - K_2(BO_2)_2$, 3) stable adiagonal cross-section XII → $LiBO_2$.

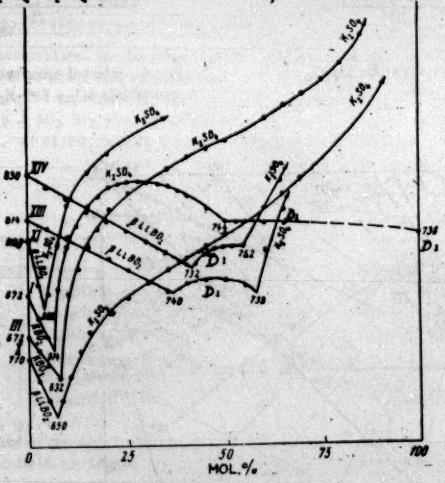


Fig. 3. Internal cross-sections at the K_2SO_4 vertex.

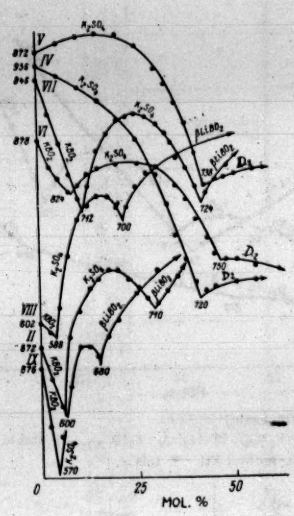


Fig. 4. Internal cross-sections at the Li_2SO_4 vertex.

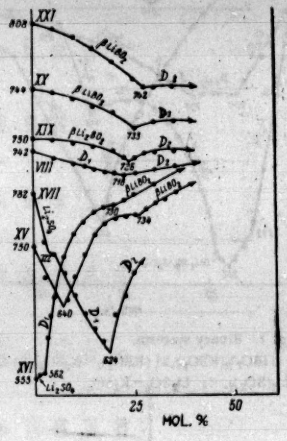


Fig. 5. Internal cross-sections at the $Li_2(BO_2)_2$ and 50% Li_2SO_4 + 50% K_2SO_4.

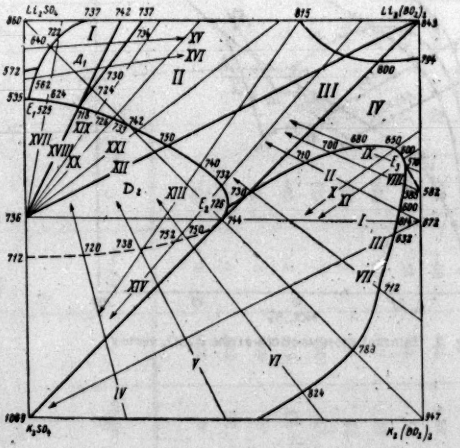


Fig. 6. Directions of inner-cross-sections of system Li, K || SO_4, BO_2.

Sections at the Li_2SO_4 vertex (Table 4, Fig 4). Section II: 50% $Li_2(BO_2)_2$ + 50% $K_2(BO_2)_2$. It has 3 branches: $K_2(BO_2)_2$, K_2SO_4, β-$Li_2(BO_2)_2$, intersecting at 600° and 6% Li_2SO_4, 710° and 29% Li_2SO_4. Section IV: 75% K_2SO_4 + 25% $K_2(BO_2)_2$. It has 2 branches: K_2SO_4 and compound D_2, intersecting at 720° and 41% Li_2SO_4. Section V: 50% K_2SO_4 + 50% $K_2(BO_2)_2$. It has 2 branches: K_2SO_4 and compound D_2, intersecting at 738° and 42.5% Li_2SO_4. Section VI: 75% $K_2(BO_2)_2$ + 25% K_2SO_4. It has 3 branches: $K_2(BO_2)_2$, K_2SO_4 and compound D_2, intersecting at 824° and 8% Li_2SO_4 and 750° and 46% Li_2SO_4. Section VII: 75% $K_2(BO_2)_2$ + + 25% $Li_2(BO_2)_2$. It has 3 branches: $K_2(BO_2)_2$, K_2SO_4 and β-$Li_2(BO_2)_2$, intersecting at 712° and 11% Li_2SO_4, 724° and 42% Li_2SO_4. Section VIII: 42.5% $K_2(BO_2)_2$ + 57.5% $Li_2(BO_2)_2$. It has 3 branches: $K_2(BO_2)_2$, K_2SO_4 and β-$Li_2(BO_2)_2$, intersecting at 588° and 4.5% Li_2SO_4 and 700° and 21.5% Li_2SO_4. Section IX: 32.5% $K_2(BO_2)_2$ + 67.5% $Li_2(BO_2)_2$. It has 3 branches: $K_2(BO_2)_2$, K_2SO_4 and β-$Li_2(BO_2)_2$, intersecting at 570° and 4% Li_2SO_4, 680° and 15% Li_2SO_4.

Sections at the $Li_2(BO_2)_2$ vertex (Table 5, Fig. 5). Section XV: 92.5% Li_2SO_4 + 7.5% K_2SO_4. It has 3 branches: Li_2SO_4, D_1 and β-$Li_2(BO_2)_2$, intersecting at 640° and 7.0% $Li_2(BO_2)_2$, 734° and 26.5% $Li_2(BO_2)_2$. Section XVI: 85% Li_2SO_4 + 15% K_2SO_4. It has 3 branches: Li_2SO_4, D_1, β-$Li_2(BO_2)_2$ intersecting at 562° and 2.5% $Li_2(BO_2)_2$ and 730° and 21% $Li_2(BO_2)_2$.

Sections at the vertex (50% Li_2SO_4 + 50% K_2SO_4). Section XVII: 90% Li_2SO_4 + 10% $Li_2(BO_2)_2$. It has three branches: Li_2SO_4, D_1 and D_2, intersecting at 722° and 8% mixture (50% Li_2SO_4 + 50% K_2SO_4); at 624° and 19.5% mixture (50% Li_2SO_4 + 50% K_2SO_4). Section XVIII: 75% Li_2SO_4 + 25% $Li_2(BO_2)_2$; branches D_1 and D_2 intersect at 718° and 22.5% mixture (50% Li_2SO_4 + 50% K_2SO_4). Section XIX: 65% Li_2SO_4 + 35% $Li_2(BO_2)_2$; branches β-$Li_2(BO_2)_2$ and D_2 intersect at 726° and 24% mixture (50% Li_2SO_4 + 50% K_2SO_4). Section XX: 55% Li_2SO_4 + 45% $Li_2(BO_2)_2$; branches β-$Li_2(BO_2)_2$ and D_2 intersect at 733° and 25% mixture (50% Li_2SO_4 + 50% K_2SO_4). Section XXI: 65% $Li_2(BO_2)_2$ + 35% Li_2SO_4; branches β-$Li_2(BO_2)_2$ and D_2 intersect at 742° and 28.5% mixture (50% Li_2SO_4 + 50% K_2SO_4).

Surface of crystallization of the system

The data accumulated for the binary systems, diagonals and internal cross-sections and for the projections of the lines of common crystallization on the plane of the polytherm of the binary system K_2SO_4–$K_2(BO_2)_2$ (Fig. 8) gave the possibility of constructing the three-dimensional liquidus diagram of the reciprocal system Li, K || SO_4, BO_2 (Fig. 7), of delineating the fields of crystallization by plotting isotherms through each 50°, and of determining the temperatures and compositions corresponding to the invariant points (Table 6).

TABLE 6

Point	t°	Composition (in %)	Equilibrium phases
E_1	525	2$Li_2(BO_2)_2$ + 80Li_2SO_4 + 18K_2SO_4	D_2, Li_2SO_4, D_1
E_2	726	51$Li_2(BO_2)_2$ + 46K_2SO_4 + 3Li_2SO_4	D_2, β-$Li_2(BO_2)_2$, K_2SO_4
E_3	570	4K_2SO_4 + 63$Li_2(BO_2)_2$ + 33$K_2(BO_2)_2$	K_2SO_4, $K_2(BO_2)_2$, β-$Li(BO_2)_2$
e_1	730	55$Li_2(BO_2)_2$ + 45K_2SO_4	β-$Li_2(BO_2)_2$, K_2SO_4
e_2	750	35$Li_2(BO_2)_2$ + 32K_2SO_4 + 33Li_2SO_4	D_2, β-$Li_2(BO_2)_2$
P_1	718	14$Li_2(BO_2)_2$ + 22K_2SO_4 + 64Li_2SO_4	β-$Li_2(BO_2)_2$, D_1, D_2

The area of the square of composition of the system is distributed in the following manner between the crystallization fields (in weight-%): potassium sulfate 43.40, compound D_2 14.93, lithium sulfate 1.23, compound D_1 3.69, lithium metaborate 27.60 (α-modification of $Li_2(BO_2)_2$ 2.51 + β-modification of $Li_2(BO_2)_2$ 25.09), potassium metaborate 9.15.

The layout of the crystallization tree of this system is represented in Fig. 9.

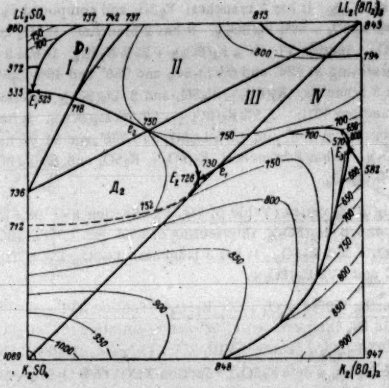


Fig. 7. Projection of the three-dimensional diagram of the reciprocal system Li, K $\|SO_4, BO_2$ on the square of composition.

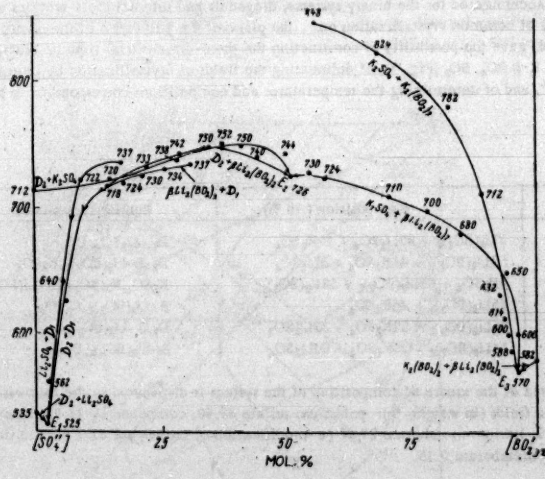


Fig 8. Projection of the curves of common crystallization on the side of the square of the reciprocal system Li, K $\|SO_4, BO_2$.

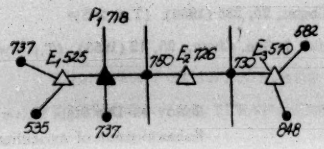


Fig. 9. Lay-out of the crystallization tree of the reciprocal system Li,K SO_4,BO_2.

Explanation in text.

The system is divided into four phase triangles by the stable diagonal $K_2SO_4-Li_2(BO_2)_2$, the stable adiagonal $D_2-Li_2(BO_2)_2$ and the cross-section XVIII extending from the 742° maximum of the complex D_1 to the maximum of the complex D_2: 1) $Li_2SO_4-D_1-D_2$, II) $D_1-D_2-Li_2(BO_2)_2$, III) $D_2-Li_2(BO_2)_2-K_2SO_4$, IV) $Li_2(BO_2)_2-K_2SO_4-K_2(BO_2)_2$. By comparing the results of investigation of the system Li,K || SO_4,BO_2 with the previously studied system [4] Li,K || WO_4,BO_2, we are able to draw generalizing conclusions from them as representatives of the sulfate and tungstate series. In the system Li,K || SO_4, BO_2 the field of the prominent complex $Li_2SO_4 \cdot K_2SO_4$ is deeply embedded, and nearly touches the stable diagonal of $K_2SO_4-Li_2(BO_2)_2$.

The corresponding tungstate complex $Li_2WO_4 \cdot K_2WO_4$ in the system Li,K || WO_4, BO_2 is not so prominent and occupies an extremely small area (1.59%).

In both systems the complexes $3LiSO_4 \cdot 2LiBO_2$ and $3Li_2WO_4 \cdot 2LiBO_2$ are also formed respectively, and are manifested in the corresponding lateral binary systems. The compound $3Li_2SO_4 \cdot 2LiBO_2$ is the more stable of the two.

It is interesting to recall the formation of an analogous complex $2LiF \cdot 3LiBO_2$ in the binary system $LiF-LiBO_2$ [2].

According to the classification of Bergman and Bukhalova [3] the general character of the system Li,K || SO_4,BO_2, shows it to be an adiagonal system with a subsidiary diagonal, whereas the tungstate system Li, K || WO_4, BO_2 is a representative of a system with a diagonal and a subordinate adiagonal.

SUMMARY

1. A study was made by the visual-polythermal method of the liquidus diagram of the ternary reciprocal system Li, K || SO_4, BO_2 and of its component binary systems $Li_2SO_4-Li_2(BO_2)_2$ and $K_2SO_4-K_2(BO_2)_2$. A compound $3Li_2SO_4 \cdot 2LiBO_2$ melting without decomposition was found.

2. The presence was established of six crystallization fields: K_2SO_4, complex $Li_2SO_4 \cdot K_2SO_4$, Li_2SO_4, $Li_2(BO_2)_2$, complex $3Li_2SO_4 \cdot 2LiBO_2$ and $K_2(BO_2)_2$.

3. The compound $Li_2SO_4 \cdot K_2SO_4$, which melts without decomposition, retains its stability also in the reciprocal system; its field is deeply embedded in the system and occupies an area of 14.9%.

4. The system is split up into four phase triangles by three triangulating sections: the adiagonal $Li_2SO_4 \cdot K_2SO_4-Li_2(BO_2)_2$, the diagonal $K_2SO_4-Li_2(BO_2)_2$ and a section extending from the 742° maximum corresponding to the compound $3Li_2SO_4 \cdot 2LiBO_2$ to the 736° maximum of the complex $Li_2SO_4 \cdot K_2SO_4$. The adiagonal section plays a decisive part in the triangulation.

5. The reaction of complex formation in the sulphate system Li, K || SO_4, BO_2 is conspicuously manifested; but in the tungstate system Li, K || WO_4, BO_2 the exchange reaction markedly predominates over the complex formation reaction.

6. The system Li, K || SO_4, BO_2 is classified as an adiagonal system with a subordinate diagonal.

LITERATURE CITED

[1] E. Nacken, N. Jahrb. Miner., Geol., Pal. B. B., 24, 43 (1907).

[2] I.I. Kitaigorodsky, T. A. Popova and O. K. Botvinkin, Bull Sector Phys. Chem. Anal., Acad. Sci. USSR, 6, 135 (1953).

[3] A. G. Bergman and G. A. Bukhalova, J. Gen. Chem., 20, 235 (1950). (T.p. 245)•

[4] A. G. Bergman, A. I. Kislova and V. I. Posypaiko, J. Gen. Chem., 25, 12 (1953). (T.p. 9)•

Received June 8, 1954

Rostov-on-Don State University and
Kuban Institute of Agriculture

• T.p. = C. B. Translation pagination.

COMPLEX FORMATION AND DOUBLE DECOMPOSITION IN THE RECIPROCAL SYSTEM OF THE TITANATES AND FLUORIDES OF SODIUM AND POTASSIUM

M. L. Sholokhovich

A considerable amount of work has been carried out in recent times on the chemical properties of the titanates of barium and lead in connection with their interesting and technically important seignetto-electrical properties [1, 2]. By contrast, very little has been published about the properties of titanates of other metals and in particular of the alkali metals. In the field of fused salts only a few papers have appeared on titanates of sodium and potassium [3, 4], while nothing at all has been published about the dielectric properties of these salts. Apart from this, a comprehensive investigation of the titanates of various metals will not only expand our knowledge of the physico-chemical properties of titanates in general, but will inevitably throw light upon the theory of seignettoelectricity.

The present investigation is the first in a series on the systematic study of the interaction of titanates of the alkali metals with other salts in melts; here we describe a method of preparation of the metatitanates of sodium and potassium and their interaction with sodium and potassium fluorides in melts. The dielectrical properties of the prepared sodium and potassium metatitanates have been examined by A. I. Khodakov in the dielectrics laboratory of the Institute of Physico-Mathematical Research of Rostov State University.

EXPERIMENTAL

The investigation was carried out by the visual-polythermal method of fusion. The tables contain a portion of the data.*

Starting substances: Sodium and potassium fluorides, "chem. pure for analysis", with m.p.s 999° (NaF) and 870° (KF); sodium and potassium metatitanates were prepared by fusion of the chemically pure respective carbonates with titanium dioxide in stoichiometrical ratios. Titanium dioxide, "pure" grade, was previously purified by prolonged digestion in 10% hydrochloric acid solution. Spectroscopic examination showed that the TiO_2 treated in this manner was free from impurities. Fusion of TiO_2 with Me_2CO_3 was conducted in an open corundum crucible in a Silit furnace. The melt was held for a long time at 1200° until CO_2 bubbles had ceased to come off. Conditions were thereby created under which the reaction $TiO_2 + Me_2CO_3 = Me_2TiO_3 + CO_2$ went substantially to completion on the titanate side. Moreover, holding at high temperature for a long period ensured formation of metatitanates from other titanates [3] that might have been formed as intermediate products. The prepared Na_2TiO_3 melted at 1025° and the K_2TiO_3 at 826°.

Binary sides (Table 1, Fig. 1). Na_2TiO_3–K_2TiO_3: layering occurs [4] in the range of 20 to 50% K_2TiO_3. We established that melts in the range of 31.5 to 50% K_2TiO_3 crystallize at very similar temperatures, so that the crystallization curve has a very sloping character. In roughly the same range a slight turbidity precedes the appearance of crystals but layering is not observed. Heterogeneity is observed, however, in rapidly cooled melts with compositions of 30 to 50% potassium metatitanate. At the same time, the crystallization curve in spite of its slope clearly points to a maximum at 906° corresponding to 1:1 composition. A melt of this composition completely solidifies at 906°. Melts containing up to 50% K_2TiO_3 completely solidify at temperatures of the order of 780°, but melts containing more than 50% K_2TiO_3 solidify at temperatures of the order of 900°. The data justify the conclusion that in the system Na_2TiO_3–K_2TiO_3 a compound $Na_2TiO_3 \cdot K_2TiO_3$ is formed which melts without decomposition at 906°. The field of this compound also appeared in the reciprocal system described below.

It may be suggested that the development of slight turbidity shortly prior to the crystallization of the compound is caused by breakdown of the compound in this region into two liquid phases. This is

* All results are expressed in equimolar percentages.

TABLE 1

1st column: percent of added salt, 2nd column: temperature of appearance of first crystals (E—eutectic)

1	2	1	2	1	2
K_2TiO_3—Na_2TiO_3		Na_2TiO_3—Na_2F_2		K_2F_2—K_2TiO_3	
0	826	0	1025	0	870
5	812	3	1005	5	868
10	798	6	973	10	860
15	798	9	958	15	852
20	830	12	948	20	844
25	852	15	930	25	835
30	873	20	895	30	826
35	886	23	898	35	817
40	890	25	899	40	806
45	900	29	894	45	798
50	906	32	886	50	788
55	906	35	880	55	776
60	906	40	907	61	764
65	904	45	940	65	777
70	910	50	958	70	782
75	934	55	967	75	790
80	958	60	978	80	798
85	966	65	982	83	806
90	996	70	986	90	811
95	1012	75	990		
		80	996	E at 50% K_2TiO_3 and 758°.	
		85	994		
		88	998		

E_1 at 13.5% Na_2TiO_3 and 784°
E_2 at 68.5% Na_2TiO_3 and 902°.

E_1 at 20% Na_2F_2 and 896°
E_2 at 35% Na_2F_2 and 880°.

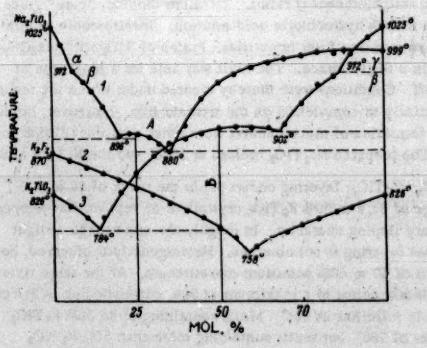


Fig. 1. Binary systems.
1) Na_2TiO_3—Na_2F_2, 2) K_2F_2—K_2TiO_3, 3) K_2TiO_3—Na_2TiO_3.
A) binary compound $3Na_2TiO_3 \cdot 2NaF$, B) binary compound $K_2TiO_3 \cdot Na_2TiO_3$.

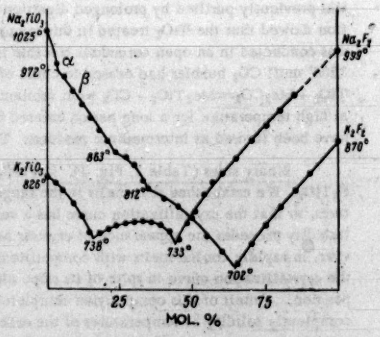


Fig. 2. Diagonal cross-sections.

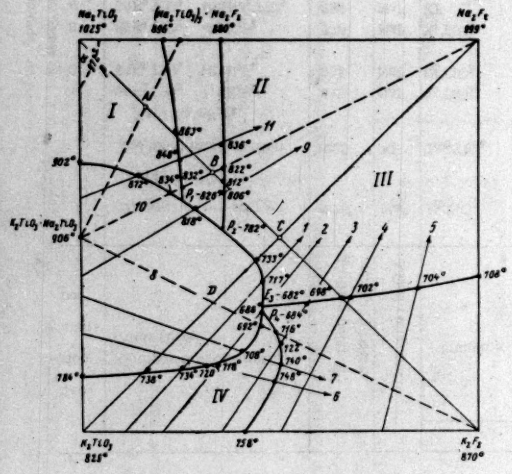


Fig. 3. Arrangement of internal sections in the system.

Explanation in text.

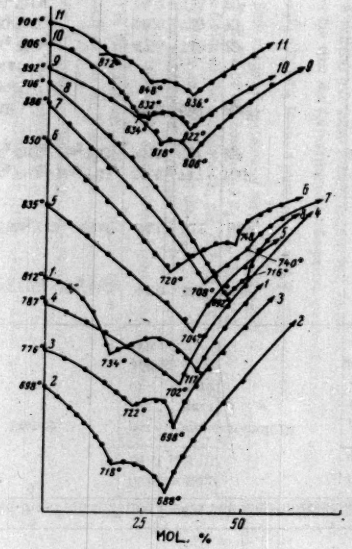


Fig. 4. Internal sections through the system.

TABLE 2

Special points of the diagonal and internal cross-sections

Section number	Composition of original melt (in %)	Melting point of original mixture	Added component	Branches of the crystallization curves and their intersections									Figure number
				Branch I	intersection of I and II: percent of added salt •	intersection of I and II: temperature	Branch II	intersection of II and III: percent of added salt	intersection of II and III: temperature	Branch III	intersection of III and IV: percent of added salt	intersection of III and IV: temperature	Branch IV	
I	Diagonal cross-section $K_2TiO_3 - Na_2F_2$	826°	NaF	K_2TiO_3	15.5	738°	$K_2TiO_3 \cdot Na_2TiO_3$	44.0	733°	NaF				2
	Diagonal cross-section $Na_2TiO_3 - K_2F_2$	1025	KF	Na_2TiO_3	23.0	863	$3Na_2TiO_3 \cdot 2NaF$	34.5	812	NaF	64.5	702°		2
1	$90K_2TiO_3 + 10K_2F_2$	812	NaF	K_2TiO_3	16.0	734	$K_2TiO_3 \cdot Na_2TiO_3$	38.0	717	NaF				3
2	$80K_2TiO_3 + 20K_2F_2$	698	NaF	K_2TiO_3	17.0	718	$K_2TiO_3 \cdot Na_2TiO_3$	35.0	688	KF	Not determined			3
3	$65K_2TiO_3 + 35K_2F_2$	776	NaF	K_2TiO_3	22.5	722	KF	32.5	698	NaF				3
4	$50K_2TiO_3 + 50Na_2TiO_3$	787	NaF	KF	34.0	702	NaF							3
5	$25K_2TiO_3 + 75K_2F_2$	835	NaF	KF	36.5	704	NaF							3
6	$75K_2TiO_3 + 25Na_2TiO_3$	850	KF	$K_2TiO_3 \cdot Na_2TiO_3$	31.0	720	K_2TiO_3	47.5	748	KF				3
7	$65K_2TiO_3 + 35Na_2TiO_3$	886	KF	$K_2TiO_3 \cdot Na_2TiO_3$	40.0	708	K_2TiO_3	50.0	740	KF				3
8	$50K_2TiO_3 + 50Na_2TiO_3$	906	KF	$K_2TiO_3 \cdot Na_2TiO_3$	45.0	692	K_2TiO_3	50.5	716	KF				3
9	$60K_2TiO_3 + 40Na_2TiO_3$	892	NaF	$K_2TiO_3 \cdot Na_2TiO_3$	28.0	818	$3Na_2TiO_3 \cdot 2NaF$	35.5	806	NaF				3
10	$50K_2TiO_3 + 50Na_2TiO_3$	906	NaF	$K_2TiO_3 \cdot Na_2TiO_3$	22.0	834	Na_2TiO_3	25.0	832	$3Na_2TiO_3 \cdot 2NaF$	35.0	822	NaF	3
11	$40K_2TiO_3 + 60Na_2TiO_3$	906	NaF	$K_2TiO_3 \cdot Na_2TiO_3$	15.0	872	Na_2TiO_3	25.0	848	$3Na_2TiO_3 \cdot 2NaF$	35.5	836	NaF	—

• Percentages are equimolecular throughout.

possible if the maximum of the compound falls below the region of the two liquid layers, i.e. the binodal curve intersects the crystallization curve of the compound. Such cases are known, even though they are rare; an example occurs in the system Mg–Ni [5].

$Na_2F_2-K_2F_2$ eutectic [6]: Our data indicate a eutectic at 60% KF and 708°.

$Na_2TiO_3-Na_2F_2$: forms a compound $3Na_2TiO_3 \cdot 2Na_2F$, melting without decomposition at 899° (Fig. 1, 1). In the region of high concentrations of sodium fluoride the melt becomes slightly turbid, evidently due to partial salting-out. It is interesting that here in the region of high concentrations of sodium fluoride the crystallization curve of NaF becomes sloping, reflecting the tendency to layering.

A similar but more clearly manifested phenomenon occurred in the system Na, K ‖ B_2O_7, Cl [7], where on the side the formation of a compound was associated with layering.

$K_2F_2-K_2TiO_3$ forms a eutectic at 59% K_2TiO_3 and 758°.

Both diagonal sections of the system (Table 2, Fig. 2) are unstable. The $K_2TiO_3-Na_2F_2$ section intersects the field of the compound $K_2TiO_3-Na_2TiO_3$. The diagonal section $K_2F_2-Na_2TiO_3$ intersects, apart from the fields of the components, the field of sodium fluoride and the field of the compound $3Na_2TiO_3 \cdot 2NaF$. There is an inflection on the Na_2TiO_3 branch of this section at 972°. A similar inflection also occurs on the branches of crystallization of sodium titanate in the binary sides $Na_2TiO_3-Na_2F_2$ and $Na_2TiO_3-K_2TiO_3$. This is possibly a polymorphic transformation of Na_2TiO_3.

The arrangement of the investigated internal sections through the system is shown in Fig. 3. Data for the sections are set forth in the corresponding Table 2 and in Fig. 4.

Fig. 5 represents the complete surface of crystallization of the system. Isotherms are plotted at intervals of 25°. The broken lines indicate the sections participating in the triangulation of the system. The system contains six crystallization fields (Table 3 and Fig. 5).

TABLE 3

Field number	Field of crystallization	Area of field (in % of total surface of system)
1	Na_2TiO_3	8.26
2	$3Na_2TiO_3 \cdot 2NaF$	5.16
3	NaF	40.72
4	$Na_2TiO_3 \cdot K_2TiO_3$	19.35
5	K_2TiO_3	8.06
6	KF	18.45

Discussion of results

Investigation of the system established the existence of the binary compounds $Na_2TiO_3 \cdot K_2TiO_3$ and $3Na_2TiO_3 \cdot 2NaF$ and showed their influence upon the double decomposition reaction.

Triangulation of the system is performed not by diagonal sections but by three unstable secants extending from the point of the compound $Na_2TiO_3 \cdot K_2TiO_3$. Consequently the compound $Na_2TiO_3 \cdot K_2TiO_3$ is a triple point in the reciprocal system. The triangulating secants are shown in Figs. 3 and 5 by broken lines. They divide the square of the reciprocal system into four co-subordinate ternary systems designated by Roman numerals in Figs. 3 and 5.

I. $Na_2TiO_3 \cdot K_2TiO_3-Na_2TiO_3-3Na_2TiO_3 \cdot 2NaF$;
II. $Na_2TiO_3 \cdot K_2TiO_3-Na_2F_2-3Na_2TiO_3 \cdot 2NaF$;
III. $Na_2TiO_3 \cdot K_2TiO_3-Na_2F_2-K_2F_2$;
IV. $Na_2TiO_3 \cdot K_2TiO_3-K_2TiO_3-K_2F_2$.

The main chemical reactions are expressed by the following equations. Two equations correspond to compositions A and B (Fig. 3) corresponding to inter-sections of the triangulating secants with the diagonal $Na_2TiO_3-K_2F_2$.

A. $5Na_2TiO_3 + K_2F_2 = K_2TiO_3 \cdot Na_2TiO_3 + 3Na_2TiO_3 \cdot 2NaF$.

This equation shows that in the melt corresponding in composition to point A a stable mixture is formed of two compounds. At point B the compound $K_2TiO_3 \cdot Na_2TiO_3$ coexists with NaF.

B. $2Na_2TiO_3 + K_2F_2 = K_2TiO_3 \cdot Na_2TiO_3 + Na_2F_2$.

The following reaction takes place at point D, corresponding to the intersection of the triangulating secant $Na_2TiO_3 \cdot K_2TiO_3 - K_2F_2$ with the diagonal $K_2TiO_3 - Na_2F_2$:

D. $2K_2TiO_3 + Na_2F_2 = K_2TiO_3 \cdot Na_2TiO_3 + K_2F_2$.

At point C, however, where the two diagonals intersect, a reaction takes place that indicates the coexistence of the compound $Na_2TiO_3 \cdot K_2TiO_3$ with sodium and potassium fluorides:

C. $2Na_2TiO_3 + 2K_2F_2 = Na_2TiO_3 \cdot K_2TiO_3 + Na_2F_2 + K_2F_2$.

The system contains four triple invariant points (Table 4).

TABLE 4

Composition and equilibrium phases of the invariant points of the system

Character of point		Temperature	Composition (in mole %)			Equilibrium phases
			KF	Na_2TiO_3	K_2TiO_3	
Triple transition	P_1	826°	25.5	59.5	15.0	$K_2TiO_3 \cdot Na_2TiO_3$; $3Na_2TiO_3 \cdot 2NaF$; Na_2TiO_3.
	P_2	782	38.0	50.5	15.5	$K_2TiO_3 \cdot Na_2TiO_3$; $3Na_2TiO_3 \cdot 2NaF$; Na_2F_2.
	P_4	684	44.5	30.5	25.0	$K_2TiO_3 \cdot Na_2TiO_3$; K_2TiO_3; K_2F_2.
Triple eutectic	E_3	682	45.0	32.0	23	$K_2TiO_3 \cdot Na_2TiO_3$; K_2F_2; Na_2F_2.

From the data of Table 4 and from the projection of the surface of crystallization of the system on the $K_2F_2 - Na_2F_2$ side (Fig. 6) we see that the invariant points into whose equilibrium phases the compound $3Na_2TiO_3 \cdot 2NaF$ enters are transition points. From this it follows that the stability of the binary compound $3Na_2TiO_3 \cdot 2NaF$, which melts without decomposition, is lowered and the compound already melts with decomposition within the system. It is interesting to note that the invariant point P_1, into whose equilibrium phases enter the components of the phase triangle I (Fig. 5), is displaced to the phase triangle III. This is illustrated with particular clarity by the scheme of the crystallization tree of the system (Fig. 7).

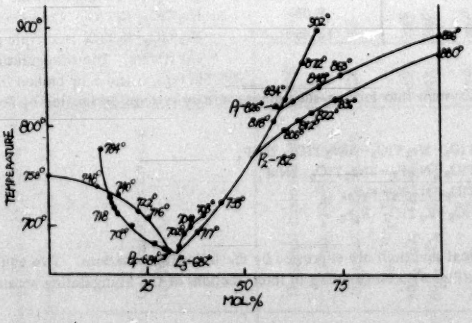
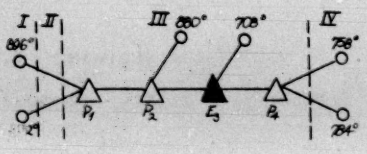


Fig. 6. Projection of the curves of common crystallization on the $K_2F_2 - Na_2F_2$ side.



○ Binary eutectic points

Fig. 7. Scheme of the crystallization tree of the system Na, K ‖ TiO_3, F.

Another interesting fact to be noted is the extremely slow temperature drop along the line of binary crystallization of $K_2F_2 - Na_2F_2$. Thus, over a range of 50% the temperature falls by only 26°, from 708 to 682°.

The investigation of the reaction of sodium and potassium titanates with sodium and potassium fluorides also confirms the hypothesis, previously mentioned [8], of the profound difference between the chemical properties of salts of sodium and potassium. Thus, potassium titanate and fluoride form a eutectic mixture, but sodium titanate and fluoride form a chemical compound which melts without decomposition.

SUMMARY

1. Sodium and potassium metatitanates have been prepared.

2. The fusion diagram of the reciprocal system Na, K ‖ TiO_3, F has been completely investigated by the visual-polythermal fusion method.

3. A 1:1 compound of sodium and potassium titanates, melting without decomposition at 906°, was detected.

4. A compound of sodium fluoride and titanate with the composition $3Na_2TiO_3 \cdot 2NaF$, melting without decomposition at 899°, was detected.

5. The boundaries, within the reciprocal system, of the fields of crystallization of the components and the compounds $Na_2TiO_3 \cdot K_2TiO_3$ and $3Na_2TiO_3 \cdot 2NaF$ were established.

6. Four ternary invariant points were found; of these one is eutectic and three are ternary transition points.

LITERATURE CITED

[1] I. N. Belyaev, M. L. Sholokhovich and G. V. Barkova, J. Gen. Chem., 24, 211 (1954). (T.p. 211)*

[2] M. L. Sholokhovich and I. N. Belyaev, J. Gen Chem., 24, 218 (1954). (T.p. 219)*

[3] P. Nigglie, Z. allg. anorg. Chem., 84, 229 (1913).

[4] Sci. Rep. Tokyo, 1, 23, 259 (1934).

[5] M. Hansen, Structure of Binary Alloys, I, II, Moscow (1941).

[6] Tech. Encyclopedia, Handb. Phys. Chem. Const., VI, 144 (1931).

[7] A. G. Bergman and N. N. Nikonova, J. Gen. Chem., 12, 460 (1942).

[8] A. G. Bergman and M. L. Sholokhovich, J. Gen. Chem., 24, 595 (1954). (T.p. 605)*

Received July 19, 1954

Rostov-on-Don State University

* T.p. = C. B. Translation pagination.

PHYSICO – CHEMICAL ANALYSIS OF THE BINARY SYSTEMS: ETHYL ALCOHOL – ANILINE, ETHYL ALCOHOL – CHLOROFORM AND CHLOROFORM – ANILINE

P. K. Migal and D. P. Belotsky

The systems studied in this research find practical application in extraction technology; for example, alcohol –chloroform mixtures are used for extraction of alkaloids. Moreover these systems are of great theoretical interest. Systems consisting of two associated compounds frequently do not reflect on the corresponding isotherms the properties of chemical compounds formed in the system due to breakdown of the associated molecules of the components.

Investigation of the thermal effects of mixing of aniline with ethyl alcohol[1] showed the formation of solvates in the system ethyl alcohol – aniline. Chemical interaction was not detected on the molecular weight composition diagram by cryoscopic determinations [2].

N. A. Izmailov[3], applying his method of calculation of the deviations of properties from additivity, and using the experimental results of a cryoscopic investigation[2], indicated the occurrence of chemical interaction in the system ethyl alcohol – aniline.

The system ethyl alcohol – chloroform was previously investigated[4] by viscosity measurements at the boiling point of mixtures, and a maximum was obtained on the viscosity/composition diagram. Measurements of molecular weight [5] did not indicate reaction between the components. The literature contains isolated data for various temperatures: surface tension at 10, 46.2 and 78.2°, density and refractive index [6]. These data again do not reveal interaction between ethyl alcohol and chlorofrom.

The system chloroform – aniline has been investigated by the fusion method[6] and by cryoscopic determinations of molecular weight[5]. On the fusion diagram the eutectic corresponds to 24 mole % aniline. The molecular weight/composition diagram only reflects breakdown of the associated molecules of aniline.

EXPERIMENTAL

Rectified ethyl alcohol was dehydrated by prolonged standing with anhydrous copper sulfate followed by boiling and by drying with metallic sodium. B. p. 78.3°, d_4^{20} 0.789, σ^{20} 22.33 dyn / cm.

Aniline (chem. pure) was stood over potassium hydroxide and then distilled over metallic sodium. The freshly distilled aniline was colorless. B.p. 183°, d_4^{20} 1.022, σ^{20} 42.85 dyn/ cm.

Chloroform (chem. pure) was washed with dilute sodium carbonate solution and partly dehydrated by freezing at below zero. It was then dried with calcium chloride and distilled in presence of a little phosphorus pentoxide. B.p. 61.2°, d_4^{20} 1.488, σ^{20} 27.20 dyn / cm.

The surface tension was measured by the method of maximum pressure of bubbles in a slightly modified apparatus[7]. The period of formation of each bubble was 5 – 7 seconds.

The solution under investigation was kept in a thermostat for 15 – 20 minutes at the required temperature, after which a manometer reading was taken. The average value of surface tension was got from 5 to 7 separate measurements. The relative error of measurement was ± 0.23%.

Viscosities were measured in viscometers of the closed type[8]; densities were determined in pycnometers (with ground-glass stoppers) of 20 ml capacity.

Surface tension, viscosity and density were measured under thermostatic conditions. Temperature fluctuations were $\pm 0.05°$. Measurements were carried out at 0, 5, 10, 15, 20 and 25°.

The refractive index was determined in a RLU refractometer at $20 \pm 0.1°$.

System ethyl alcohol – aniline. The surface tension isotherms of the system ethyl alcohol – aniline, obtained at the above –mentioned temperatures in the concentration range of 0 to 100 mole % of each component, are shown in Fig. 1. From the alcohol to the aniline side the curves are at first slightly concave in relation to the axis of compositions, and at 70 mole% the concavity is smoothed away; the curves gradually become convex and, starting from 20 mole% alcohol and extending to pure aniline, the curves again become concave.

The surface tension isotherms of the system alcohol – aniline are not altogether consistent with the interpretation of the bulging of the isotherms [9, 10].

As indicated above, the plotted isotherms are only concave to the axis of composition in the vicinity of the pure components, the concavity being reversed toward the middle of the curve. It may be suggested that the slight rise in the curves on approach to the pure component may be explained by solvation of the molecule of one component by molecules of the other, while the sagging of the curve may be due to chemical interaction of the components with formation of a 1:1 compound.

The viscosity isotherms of the system are shown in Fig. 2. We see that with rising temperature the isotherms become straighter so that at 25° the viscosity curve is almost rectilinear.

Two opposing processes take place simultaneously in the system: formation of a compound that increases the viscosity, and breakdown of the associated molecules which promotes a fall of viscosity. It must be assumed that breakdown of associated molecules predominates when one component dissolves in the other, due to which the viscosity isotherms lack the characteristic indication of a chemical compound.

The isotherms of specific volume (when expressing the composition in weight - percent) of the system ethyl alcohol – aniline are convex to the axis of composition, which indicates contraction in the system. In Fig. 3. (Curves I) are shown the specific volume isotherms at 0 and 20°.

The refractive index isotherm (Fig. 4, curve II), in spite of the great difference from the refractive indices of the components, has a marked concavity to the axis of composition.

System ethyl alcohol – chloroform. The surface tension isotherms of the system ethyl alcohol – chloroform are concave to the axis of composition and retain the same shape over the whole interval of temperatures (Fig. 5). They deviate to an insignificant extent from the isotherms of a normal system. This insignificant deviation, characterized by a slight concavity to the axis of composition, may be explained by the fact that the component (chloroform) with the greater surface tension has a lower dielectric constant and a smaller dipole moment. With such a relation of dipole moments and surface tensions, the curve is bound to be concave to the axis of composition[10], in agreement with our results.

The viscosity isotherms, as shown in Fig. 6, are convex to the axis of composition and are consequently characteristic of system without chemical interaction. As was indicated above, we previously studied this system by viscosity measurements [4] at the boiling points of the mixtures. According to these data the maximum on the viscosity/composition diagram at an alcohol concentration of 80 mole% is evidently due to the more rapid fall of viscosity of the alcohol in comparison with its mixtures with chloroform.

Results of measurements of specific volume, plotted in Fig. 3 (curves II), show that the specific volume isotherms at 0 and 20° are straight lines; this is characteristic of the absence of a volume change on mixing of the components of a system.

The refractive index isotherms for 20° (Fig. 4, curve I) are very slightly concave to the axis of composition.

Applying the cryoscopic data of V. V. Udovenko[7], we calculated the deviation of the cryoscopic depression additivity by the method of N. A. Izmailov[3]. The calculated and the experimental curves entirely coincide. Coneequently in this system reaction between components is likewise not detected by the cryoscopic method.

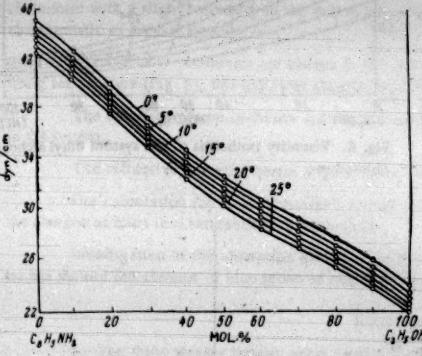


Fig. 1. Surface tension isotherms of the system ethyl alcohol – aniline.

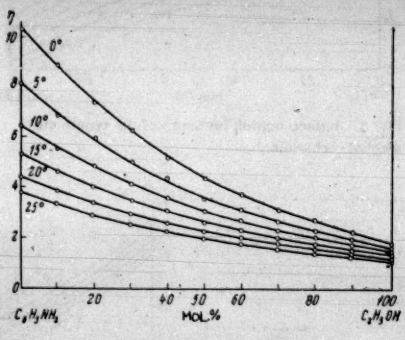


Fig. 2. Viscosity isotherms of the system ethyl alcohol – aniline.

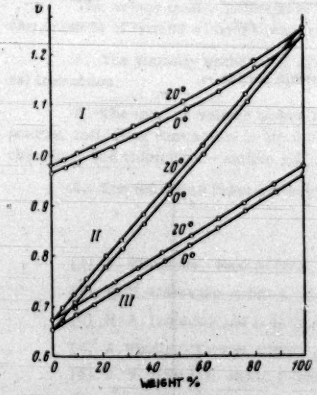


Fig. 3. Specific volume isotherms at 0 and 20°.
I) ethyl alcohol – chloroform; II) ethyl alcohol – aniline; III) aniline – chloroform.

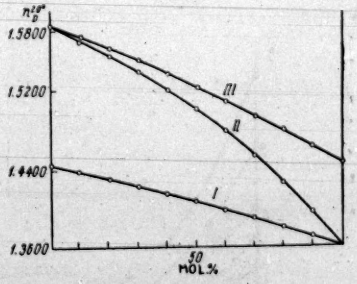


Fig. 4. Refractive index isotherms at 20°.
I) ethyl alcohol – chloroform; II) ethyl alcohol – aniline; III) aniline – chloroform.

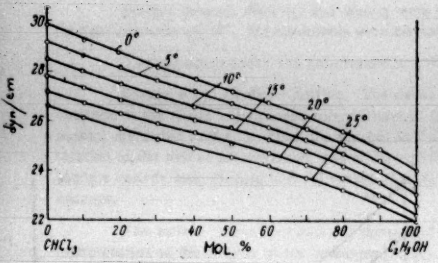


Fig. 5. Surface tension isotherms of the system ethyl alcohol – chloroform.

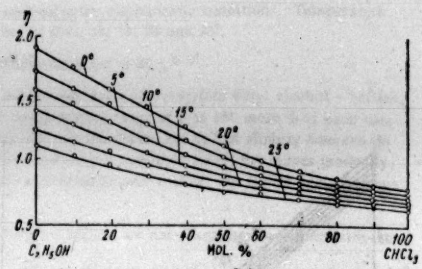


Fig. 6. Viscosity isotherms of the system ethyl alchol – chloroform.

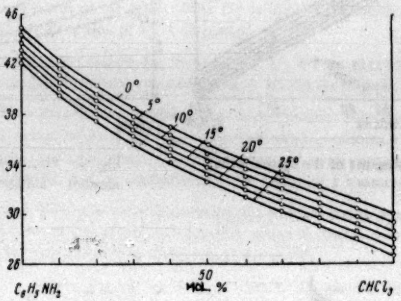


Fig. 7. Surface tension isotherms of the system aniline – chloroform.

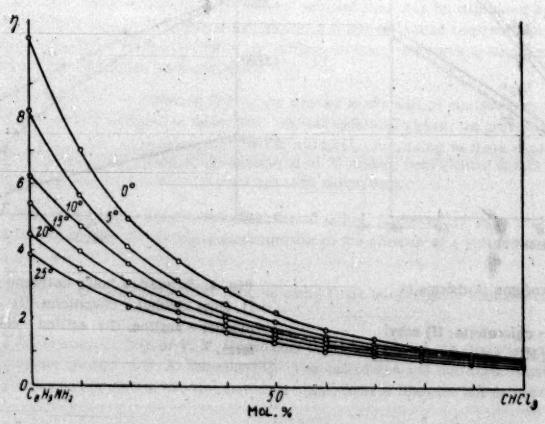


Fig. 8. Viscosity isotherms of the system chloroform – aniline.

A Raman spectrographic investigation[11] established the occurrence of slight interaction in the system methyl alcohol – chloroform due to formation of a hydrogen bond. It is not manifested, however, in appreciable excitation of the vibrations of the O–H groups but only restricts the freedom of orientation of the molecules of alcohol in relation to one another. This consideration may also be applied to the system ethyl alcohol – chloroform, especially since ethyl alcohol is less active than methyl alcohol.

System chloroform – aniline. The surface tension isotherms (Fig. 7) fall smoothly from aniline to cholroform with a slight convexity to the axis of composition. This course of the surface tension curve is characteristic of normal systems.

The viscosity isotherms are convex to the axis of composition and approach rectilinearity with rising temperature (Fig. 8); this indicates absence of chemical interation in the system.

The specific volume isotherms are straight lines (Fig. 3, III), indicating the absence of contraction in the system.

The refractive index isotherms (Fig. 4, curve III) are very slightly concave to the axis of composition.

Our calculation (by N. A. Izmailov's method) of the cryoscopic data of V. V. Udovenko[5] also showed the absence of chemical interactioni in the system.

Investigation of the absorption spectra of aniline and chloroform[12] by the method of differential spectra has showed the absence of interaction of chloroform with aniline.

SUMMARY

1. The three ternary systems ethyl alcohol–aniline, ethyl alcohol – chloroform and chloroform – aniline were investigated by measurements of surface tension, viscosity and density at 0, 5, 10, 15, 20 and 25°, and by measurements of refractive index at 20°.

2. The surface tension isotherms of the system ethyl alcohol – aniline exhibit a sag which indicates formation of a chemical compound of 1:1 composition.

The surface tension isotherms of the systems ethyl alcohol – chloroform and chloroform – aniline are characteristic of systems without chemical interaction.

3. The viscosity isotherms of all three systems have the form characteristic of systems without chemical interaction.

4. The specific volume isotherms of the system ethyl alcohol – aniline are convex to the axis of composition, indicating contraction in the system, while the specific volume isotherms of the systems ethyl alcohol – chloroform and chloroform – aniline are straight lines.

5. The refractive index isotherms are concave to the axis of compositions for all three systems.

LITERATURE CITED

[1] V. Timofeev. Heat of Formation of Nonaquecus Solutions. Kiev (1905).

[2] V. V. Udovenko and S. F. Babak, J. Gen. Chem., 18, 572 (1948).

[3] N. A. Izmailov and L. L. Spivak, Sci. Memoirs Kharkov State Univ., 7, 153 (1950).

[4] A. Findlay, Z. phys. Chem., 69, 203 (1909).

[5] V. V. Udovenko and S. F. Babak, J. Gen. Chem., 17, 1583 (1947).

[6] Tech. Encyclopedia, Handb. Chem. Phys. and Tech. Constants, X, 55 (1933).

[7] S. N. Aleshin, Factory Lab., 33, No. 4, 497 (1949).

[8] Kh. Khalinova, J. Tech. Phys., 8, 1249 (1938).

[9] N. A. Trifonov, Nature USSR, No. 1, 38 (1934).

[10] N. A. Trifonov, Proc. Acad. Sci. USSR, 55, 41 (1947).

[11] V. I. Malyzshev, Bull. Acad. Sci. USSR, Div. Phys. Sci., 5, 13 (1941).

[12] N. G. Yaroslavsky, J. Phys. Chem. USSR, 22, 256 (1948).

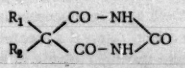
Received September 12, 1954

Chernovits State University

COMPLEX COMPOUNDS OF COPPER WITH DERIVATIVES OF BARBITURIC ACID AND PYRIDINE

Ya. A. Fialkov and L. I. Rapaport

Derivatives of barbituric acid (barbiturates)



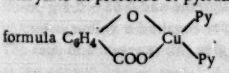
are capable of forming colored complex compounds with cations of a series of heavy metals. With salts of copper and certain other metals in presence of pyridine, barbiturates form mono-and disubstituted complexes of the type of:

I. $(barb.')_2M \cdot Py_2$, in which (barb.') is a barbiturate in the form of an anion of a monobasic acid; M is Cu, Cd, Mn or Ag_2; Py is pyridine.

II. (barb.") $M \cdot Py_2$, in which (barb.") is an anion of a barbiturate as dibasic acid; M is Cu, Ni or Ag_2.

Monosubstituted complex salts (I) were obtained for veronal [1]; for luminal, both monosubstituted salts were obtained (I) – by addition to a solution of luminal-sodium of cupric chloride and pyridine-and disubstituted salts (II) – by addition of the same reactant to a solution of 1 mole luminal containing 2 moles sodium hydroxide [2].

Formation of these complexes lies at the basis of one of the reactions for detection of barbiturates [3].

Similar complex compounds of copper are also known for other organic acids. Thus, for example, V. I. Kuznetsov [4] reacted benzoates of alkali metals with copper salts in presence of pyridine and obtained the complex $CuPy_2(C_6H_5COO)_2$. A. K. Babko and co-workers [5-7] closely investigated the system copper – pyridine – salicylate by measurement of the extinction of color of solutions containing ions of copper and salicylate in presence of pyridine. He determined the composition and assigned to the complex the structural formula 

The reaction with pyridine and copper sulfate was tested by Garratt [8] for quantitative determination of veronal, but without success. According to Garratt the composition of the separated precipitate, calculated form the copper content, did not correspond to the formula Cu $(barb.')_2 \cdot Py_2$. An appreciable amount of barbiturate remained in the filtrate.

The presence of the grouping CONHCONHCO has a great influence upon the chemical properties of barbituric acids. It endows barbiturates with the ability to undergo amido-imido tautomerism with formation of one or two $-C(OH)=N-$ groups which intensify the acidic character of barbiturates. This circumstance, as also the presence of electron donators (atoms of nitrogen and oxygen), creates favorable conditions for formation of inner-complex salts of barbiturates of diverse composition.

Barbiturates are very weak acids with a dissociation constant of the order of 10^{-7}–10^{-8} [9]; therefore the process of interaction of barbiturates with salts of heavy metals is bound to be greatly influenced by

the pH of the reaction medium. Rise of the pH into the strongly alkaline region displaces the tautomeric equilibrium and enables barbiturates to react like dibasic acids, a property that may not be reflected in the composition of the complexes.

In this connection we undertook experiments on the preparation of copper – pyridine complex compounds of barbiturates in presence of 1 or two moles sodium hydroxide per mole barbiturate, and in some cases with excess of alkali.

EXPERIMENTAL

The following barbiturates were selected for study of the influence of substituents in the barbituric acid ring at the carbon in the 5-position and at the nitrogen: a) 5,5-diethyl-barbituric acid (veronal), b) 5,5-phenyl-ethyl-barbituric acid (luminal), c) 5,5-ethyl-isoamyl-barbituric acid (amytal), d) 5,5-isopropyl-β-bromoallyl-N-methyl-barbituric acid (acid form of pronarcone). The amount of copper sulfate taken in preparing the complexes corresponded to 1 – 2 moles per mole barbiturate. Pyridine was taken in the amount of 4 to 10 moles per mole barbiturate.

Monosubstituted copper-pyridine complexes were obtained in the following manner: to a weighed quantity of the acidic form of the barbiturate (3 – 5 g) or its monosubstituted sodium salt• was added 10 ml pyridine and a 0.5 N solution of $CuSO_4$. After a short interval a precipitate came down and was isolated as described above. Since amytal is very much more sparingly soluble in water than veronal and evidently reacts slowly with copper sulfate, a mixture of the complex and unreacted amytal comes down under the conditions of such an experiment. The amytal is removed by washing the previously dried precipitate with ether.

The same procedure was applied to preparation of disubstituted complexes with the difference that to the weighed sample of acid form of barbiturate was added 2 – 2,3 moles sodium hydroxide. The resultant precipitates usually contain a small amount of copper hydroxide. By addition of ammonium chloride (2 –2.5 g) the $Cu(OH)_2$ can be converted into a soluble complex $[Cu(NH_3)_2(H_2O)_2]Cl_2$, after which the precipitate is treated as described above.

For quantitative analysis the prepared complexes were first decomposed with 1 N sulfuric acid solution. The barbiturate was extracted with ether and after evaporation of the solvent it was titrated with a solution of NaOH or $AgNO_3$; copper was determined iodometrically. Pyridine was determined by running an exact amount of 1 N sulfuric acid solution into a weighed sample of complex and by titrating the excess of the former with alkali solution (indicator consisting of 3 drops dimethylaminoazobenzene solution and 1 drop methylene blue). The difference between the amount of acid consumed in the overall reaction with copper and pyridine and the doubled•• amount of $Na_2S_2O_3$ solution consumed in the iodometric titration of the copper corresponds to the content of pyridine in the weighed sample of complex.

The presence of water of crystallization was detected in the following manner: 0.8 – 1 g preparation was placed in a test tube which was closed with a stopper and heated (over a spirit lamp) until the preparation decomposed. The drops of liquid condensing on the sides of the test tube were taken up on a strip of filter paper. The latter was transferred to another test tube to which was added 1 – 2 ml ligroine and 0.05 – 0.1 g potassium bichromate; it was then gently shaken. In presence of water the filter paper acquired a yellow color. The intensity of the color is proportional to the water content. Pyridine does not give this reaction and does not interfere with the water determination.

In the table are set forth the results of analysis of the preparations obtained with definite ratios of reactants; their physical properties are listed and also the solubility data for the complexes in chloroform. These complexes are insoluble or very poorly soluble in water, alcohol, ethyl ether and acetone. Chloroform solutions of the complexes with veronal and amytal do not conduct current.

Inorganic acids decompose copper-pyridine complexes of barbiturates with liberation of the free barbituric acids according to the scheme:

$$[Cu(\text{barb.}')_2 \cdot Py_2] + 2H_2SO_4 = 2(\text{barb.}'H) + CuSO_4 + (C_5H_5NH)_2SO_4.$$

Solutions of caustic alkalies also decompose these complexes with formation of cupric hydroxide:

• Prepared form the acidic form by addition of an equimolar amount of NaOH

•• Due to the difference in gram-equivalents of copper in the reaction with sulfuric acid and in the iodometric determination.

$$[Cu(barb.')_2 \cdot Py_2] + 2NaOH = 2\ barb.'\ Na + Cu(OH)_2 + 2C_5H_5N.$$

With excess of ammonia solution, copper ammine is formed and pyridine is liberated:

$$[Cu(barb.')_2 \cdot Py_2] + 6NH_3 + 2H_2O = [Cu(NH_3)_4](OH)_2 + 2\ barb.'\ NH_4 + 2C_5H_5N.$$

The disubstituted complexes of barbiturates react similarly.

EVALUATION OF RESULTS

The experimental data presented in the table show that two types of complexes can be obtained by interaction of copper salts with barbituric acids—mono- and disubstituted salts of barbiturates, depending upon the molar ratio of sodium hydroxide and barbiturate. In experiments with the acidic forms of barbiturates (in the absence of caustic alkali), veronal, luminal and amytal form monosubstituted complexes with the general formula $Cu(barb.')_2 \cdot Py_2$. In experiments with equimolar ratio of sodium hydroxide to barbiturate, such complexes could be obtained for luminal, amytal• and pronarcone.

In cases when 2 moles of sodium hydroxide per mole barbiturate participate in the preparation of the copper-pyridine complexes of barbiturates, disubstituted salts are formed with luminal Cu (lumin.") · · Py · H_2O••, veronal Cu (veron.") · $Py_2 \cdot 2H_2O$, and amytal Cu (amyt.") · $Py_2 \cdot 2H_2O$•••.

Formation of only monosubstituted salts of pronarcone with participation of both 1 and 2 moles of sodium hydroxide must be attributed to the fact that in the molecule of this barbiturate the hydrogen of one of the imido groups is substituted by a methyl group which rules out the possibility of formation of disubstituted salts.

A phenomenon of opposed character was observed in experiments with veronal: independently of the molar ratio of sodium hydroxide to barbiturate (1:1 or 2:1), only the disubstituted salt was obtained Cu (veron.") · $Py_2 \cdot nH_2O$ (n = 2 or 3).

We suggest that this behavior is due to the considerably greater solubility of the monosubstituted salt. Moreover, the reaction of formation of copper-pyridine complexes of veronal is very sensitive to an increase of the pH of the medium, and therefore the monosubstituted salt Cu (veron.') · Py_2 could only be obtained from the acidic form – without addition of alkali. A similar but considerably weaker effect of alkali was manifested also in the experiments with amytal; on addition of 1 mol sodium hydroxide to 1 mol barbiturate, as in the experiments with the acidic form, the monosubstituted salt $Cu(amyt.')_2 \cdot Py_2$ is formed, but together with a small amount of the disubstituted salt.

The composition of the complexes is not affected by excess of copper sulfate up to double or even up to four times the amount in relation to the stoichiometric ratio (in experiments on preparation of monosubstituted salts).

The physical properties of copper-pyridine complexes of barbiturate compounds [vivid, bright or dark-lilac color not characteristic of salts of divalent copper, the relatively high temperature of decomposition or melting of the complexes, the insolubility in water, alcohol, ether and acetone, and the solubility in chloroform (with exception of luminal derivatives)] entitle us to class these compounds as inner-complex salts. The copper in them is linked to the nucleus of the barbiturates, while the pyridine molecules are coordinated at the central copper atom. A similar phenomenon – coordination of polar molecules at the central atom of inner-complex salts – is encountered in a series of other complexes, for example acetylacetonates [10].

Addition of pyridine to copper is reflected in the color of the salts. Precipitates of copper barbiturates, formed by reaction of $CuSO_4$ with sodium salts of barbituric acids, are usually green. On running pyridine into these precipitates, they acquire a lilac color. The structure of monosubstituted complex salts of barbituric acids

• The slightly high content of copper in the prepared complex in comparison with the calculated value for Cu (amyt.')$_2 \cdot Py_2$ and the correspondingly low content of amytal and nitrogen can be evidently accounted for by the formation under the experimental conditions of a small amount of the disubstituted salt Cu (amyt.") · · Py_2 in the approximate ratio of 6:1.

•• According to [2] a complex with the composition Cu (lumin.") · Py_2 was obtained.

••• The slightly high content of copper and amytal and the lower content of pyridine and nitrogen in this complex (see table) can be explained by the presence in the analyzed salt of a trace of the complex Cu (amyt.") · · Py · H_2O.

TABLE

Copper-pyridine Complex Compounds of Barbiturates

Formula	Moles taken per mole barbiturate		Results of analysis (in %)			
			copper		barbiturate	
	NaOH	$CuSO_4$	found	calculated	found	calculated
Luminal						
$Cu(C_{12}H_{11}O_3N_2)_2 \cdot Py_2$	--	1.0	9.60	9.30	67.20	67.59
	1.0	1.0	9.50		67.60	
	1.0	2.0	9.45		67.40	
$Cu(C_{12}H_{10}O_3N_2) \cdot Py \cdot H_2O$	2.0	1.0	16.10	16.26	59.60	58.89
	2.0	1.0	16.20		58.50	
	2.3	1.0	16.30		59.10	
Veronal						
$Cu(C_8H_{11}O_3N_2)_2 \cdot Py_2$	--	1.2	10.77	10.80	62.17	62.29
$Cu(C_8H_{10}O_3N_2) \cdot Py_2 \cdot 3H_2O$	1.0	1.2	13.60	13.88	40.70	40.00
	1.0	1.2	13.70		40.80	
$Cu(C_8H_{10}O_3N_2) \cdot Py_2 \cdot 2H_2O$	2.0	1.2	14.60	14.44	41.80	41.41
	2.0	1.2	14.63		41.80	
	2.2	1.2	14.71		41.80	
Amytal •••						
$Cu(C_{11}H_{17}O_3N_2)_2 \cdot Py_2$	--	1.9	9.42	9.45	67.40	67.01
	1.0	1.9	10.80		63.90	
	1.0	1.9	10.70		63.40	
$Cu(C_{11}H_{16}O_3N_2) \cdot Py_2 \cdot 2H_2O$	2.0	1.9	13.70	13.18	50.10	46.53
	2.0	1.9	14.00		50.50	
Pronarcone						
$Cu(C_{11}H_{14}O_3N_2Br)_2 \cdot Py_2$	1.0	2.0	7.90	7.69	72.30	73.15
	1.0	2.0	8.06		72.00	
	2.0	2.0	8.05		72.50	

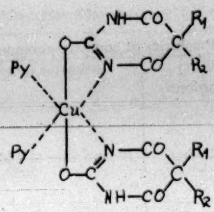
••• The compounds amytal and pronarcone were prepared for the first time by us.

Results of analysis (in %)				Properties of complex compounds		
pyridine		nitrogen		color	solubility in chloroform	behavior in heating ••
found	calculated	found	calculated			
22.60	23.12	11.90	12.28	Bright lilac	Insoluble	Decomposes at 244-246°
22.50		12.10				
22.70		–				
21.20	20.23	10.75	10.74	Coffee•	Insoluble	Decomposes at 255-257°
20.50		–				
20.60		10.75				
24.37	26.89	–	–		1: 500	Turns green at 220°, decomposes at 235-237°
34.20	34.56	12.20	12.28	Bright lilac	1: 200	Turns green at 150°, decomposes at 260-263°
34.50		–				
33.80	35.95	12.40	12.73	Dark-violet	1:150	Turns green at 150° and decomposes at 238-241°
34.00		–				
33.50		12.30				
24.27	23.53	–	12.50	Lilac	1:50	Decomposes at 208-210°
23.20		12.05				
23.50		–				
29.60	32.82	10.85	11.62	Dark lilac	1: 20	Partly melts at 197-200° with decomposition
29.10		–				
19.83	19.15	–	–	Dark-violet	–	M.p. 201-203°
19.60		–				
19.60		–				

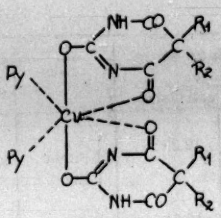
• The original dark-lilac color changes when salt is dried in a desiccator and becomes coffee-color.

•• In all cases pyridine was evolved on heating to the specified temperature.

can evidently be represented by one of the following two formulas (R_1 and R_2 – are hydrocarbon radicals):

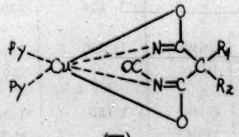


(I)



(II)

For disubstituted copper-pyridine complexes of barbiturates the structural formula (III) may be proposed:



(III)

The coordination number of copper in these complexes is 6. The water molecules in complexes containing, apart from 2Py, 2 or 3 H_2O are apparently combined through hydrogen bonds.

The following experimental data permit an approximate evaluation of the stability of the above-described complex compounds. These compounds are precipitated in presence of pyridine, present even in considerable excess; consequently their instability constant is lower than the instability constant of $[CuPy_2]^{2+}$, which is $8 \cdot 10^{-5}$ [6].

According to the data of A. K. Babko [11] the dissociation constant of Cu (or CuSal") is $2.3 \cdot 10^{-11}$. This salicylate complex displaces pyridine form the inner sphere of the pyridine complex of copper $[CuPy_2]^{2}$, afterwards combining with it with formation of a ternary compound Cu (Sal.") $\cdot Py_2$. We have established that on addition of barbiturate to a solution of Cu (Sal.") $\cdot Py_2$, the complex Cu (barb.')$_2 \cdot Py_2$ is precipitated. This must be due to displacement of salicylate ions from the complex Cu (sal.") $\cdot Py_2$ and their replacement by barbiturate ions. This indicates that the instability constant of the complex Cu (barb.')$_2 \cdot Py_2$ is lower than the instability constant of Cu (Sal.") $\cdot Py_2$.

In presence of ammonia solution, however, copper-pyridine complexes of barbiturates are not formed; this is evidence that the instability constants of the prepared complexes are higher than the instability constant of copper ammine $[Cu(NH_3)_4]^{2+}$ ($K = 2 \cdot 10^{-13}$) [12]. We can therefore conclude that the instability constant of the complex Cu (barb.')$_2 \cdot Py_2$ is in the range of $10^{-11} - 10^{-13}$.

Consequently it may be postulated that complex compounds of copper with barbiturates and pyridine must be regarded as complexes of relatively poor stability. Evidence in support of this is their decomposition by solutions of inorganic acids, caustic alkalies and ammonia.

Results of experiments on preparation and investigation of complex compounds of copper with barbiturates and pyridine are also of practical value, since a method of quantitative determination of certain barbiturates has been developed on their basis. This method consists in precipitation of copper-pyridine complexes of barbiturates, using excess of titration solution of copper sulfate, followed by iodometric titration of this excess.

SUMMARY

1. A study was made of the process of chemical interaction of barbiturates – luminal, veronal, amytal and pronarcone – with salts of divalent copper in presence of pyridine.

2. Conditions were established in which are formed both monosubstituted copper-pyridine salts of barbiturates of the general formula Cu (barb.')$_2$ · Py$_2$ and disubstituted salts Cu (barb.")· Py$_2$, usually crystallizing 2 or 3 molecules of water.

3. The prepared copper-pyridine complexes of barbiturates are inner-complex salts with a copper coordination number of 6.

LITERATURE CITED

[1] J. Zwikker, Chem. Zentr., 1932, I, 109; 1932 II, 3895.

[2] R. Cernatescu, Vascautanu, Anal. Sci. Univ. Jassy, 25, 9 (1939); 23, 356 (1937).

[3] K. Bauer, Analysis of Organic Compounds. I. L., 343 (1953).

[4] V. I. Kuznetsov, J. Anal. Chem. USSR, 2, 67 (1947).

[5] A. K. Babko, Bull. Sector Plat. Acad. Sci. USSR, 26, 163 (1951).

[6] A. K. Babko, Bull. Sector Plat. Acad. Sci. USSR, 26, 163 (1951).

[7] A. K. Babko and M. M. Tananaiko, J. Gen. Chem., 23, 1459 (1953). (T.p. 1525)•

[8] D. C. Garratt. Drugs and Chemicals, Their Quantitative Analysis. London, 36 (1937).

[9] M. E. Krahl, Chem. Zentr., 1940, II, 2144.

[10] A. Werner, New ideas in the Field of Inorganic Chemistry. Khimteoret, 281 (1936).

[11] A. K. Babko, J. Gen. Chem., 17, 443 (1947).

[12] A. A. Grinberg, Introduction to the Chemistry of Complex Compounds. State Chemical Publishing House, 359 (1951).

Received October 30, 1954

Central Laboratory of Pharmaceutical Research
Ministry of Public Health of the Ukrainian SSR

• T.p. = C. B. Translation pagination.

A NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHINIC AND THIOPHOSPHINIC ACIDS•

XXIII. ADDITION OF PHOSPHONOACETIC ESTER, PHOSPHONOACETONE AND ITS HOMOLOGS TO UNSATURATED COMPOUNDS

A. N. Pudovik and N. M. Lebedeva

In the preceding communications [1,2] we showed that phosphonoacetic ester, containing mobile hydrogen atoms in the methylene group, is capable of adding on to esters and nitriles of various α, β-unsaturated carboxylic acids and to α, β-unsaturated ketones, and of entering into condensation reactions with aromatic aldehydes. Additions of phosphonoacetic ester and its homologs to electrophilic reactants has also been reported by Mikhakski and Fischer [3]. They obtained products of addition of phosphonoacetic ester to acrylonitrile and ethyl cinnamate, and of butylphosphonoacetic ester to methyl acrylate and acrylonitrile. In all these reactions phosphonoacetic ester behaves like malonic and acetoacetic esters. However, its reactivity, especially in condensation reactions, is low due to the weak electrophilic properties of the phosphono group.

In the present investigation we realized the addition of phosphonoacetic ester to a series of nitriles and esters of unsaturated carboxylic acids.

Performance of the reaction between phosphonoacetic ester and methyl acrylate in presence of excess of the latter led to products of addition to one and two molecules of unsaturated ester – the methyl ester of α-diethylphosphono-glutaric acid and the dimethyl ester of γ-diethylphosphono-γ-carboxyethyl-pimelic acid in total yield of 81.5%:

$$(C_2H_5O)_2\overset{\overset{O}{\|}}{P}CH_2COOC_2H_5 + 3CH_2{=}CH{-}COOCH_3 \xrightarrow{C_2H_5ONa}$$

$$\longrightarrow (C_2H_5O)_2\overset{\overset{O}{\|}}{P}\overset{\overset{COOC_2H_5}{|}}{C}HCH_2CH_2COOCH_3 + (C_2H_5O)_2\overset{\overset{O}{\|}}{P}\overset{\overset{COOC_2H_5}{|}}{C}(CH_2CH_2COOCH_3)_2.$$

The reaction was conducted in presence of sodium ethoxide and went with considerable heat development in the reaction mixture. The prepared esters a colorless, viscous liquids, readily soluble in alcohol, ether and other organic solvents; they have limited solubility in water and exhibit surface activity in relation to water. The addition of phosphonoacetic ester to ethyl crotonate and ethyl cinnamate goes less energetically. In both cases we succeeded in isolating only one product: the diethyl ester of α-diethylphosphono-β-methylglutaric acid and the diethyl ester of α-diethylphosphono-β-phenylglutaric acid.

Reaction of phosphonoacetic ester with methacrylonitrile and vinylacetonitrile went very much more slowly than with acrylonitrile. On the analogy of the additions of dialyl phosphorous acids [4], we assumed that in the case of addition of phosphonoacetic ester in presence of alkoxyl anions, vinylacetonitrile isomerizes to the thermodynamically more stable crotonitrile:

$$CH_2{=}CHCH_2CN \xrightarrow{OC_2H_5^-} CH_3CH{=}CHCN \xrightarrow{(C_2H_5O)_2\overset{\overset{O}{\|}}{P}CH_2COOC_2H_5}$$

$$\longrightarrow (C_2H_5O)_2\overset{\overset{O}{\|}}{P}\overset{\overset{COOC_2H_5}{|}}{C}HCH\overset{\overset{CH_3}{|}}{C}H_2CN.$$

• Preceding communication, see [1].

The reaction gives the ethyl ester of α-diethylphosphono-β-methyl-γ-cyanobutyric acid. The constants, yields and analyses of the synthesized compounds are detailed in Table 1. Saponification of some of the prepared substances did not lead to satisfactory results; the corresponding acids are viscous, colorless or faint-yellow liquids, which do not crystallize on standing for some months.

TABLE 1.

Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Analysis for P (in %)		Yield (in %)
				found	calculated	found	calculated	
$(C_2H_5O)_2PCHCH_2CH_2COOCH_3$ O $COOC_2H_5$	167–168°(2)	1.4410	1.1368	72.04	71.79	9.75, 9.65	10.00	81.5
$(C_2H_5O)_2PC(CH_2CH_2COOCH_3)_2$ O $COOC_2H_5$	199–200(1)	1.4550	1.1712	91.75	91.91	7.90, 7.91	7.83	
$(C_2H_5O)_2PCHCH(CH_3)CHCOOC_2H_5$* O $COOC_2H_5$	–	–	–	–	–	9.35	9.26	17
$(C_2H_5O)_2PCHCH_2CH(CH_3)CN$ O $COOC_2H_5$	166–167(2.5)	1.4418	1.1045	69.72	69.95	10.91, 11.00	10.65	22.0
$(C_2H_5O)_2PCHCH(CH_3)CH_2CN$ O $COOC_2H_5$	164(4)	1.4458	1.1144	69.61	69.95	10.61, 10.71	10.65	67.8

The study of the properties of the phosphorus-containing analog of acetoacetic ester – phosphonoacetone – was continued. We synthesized phosphonoacetone, according to [5], by the action of bromoacetone on triethyl phosphite. For reactions we used a product with b.p. 126–127° (9mm) and n_D^{20} 1.4345. We performed the alkylation of phosphonoacetone by acting with alkyl halides on its sodium and potassium derivatives. Formation of metallic derivatives of phosphonoacetone takes place slowly and incompletely due to their poor solubility in ether. This creates definite difficulties for isolation of the alkylation products since their boiling point is very close to that of phosphonoacetone. Methyl and ethyl derivatives of phosphonoacetone were obtained in yields of about 45%.

Addition of phosphonoacetone and its homologs to unsaturated compounds was accomplished by the general method in presence of an alkaline catalyst. We have preciously effected the addition of phosphonoacetone to acrylonitrile when products of addition to one and two molecules of acrylonitrile were obtained. In the present investigation we added phosphonoacetone to methyl acrylate, diethyl maleate, diethyl acetylenedicarboxylate and ethylideneacetone; we also added ethylphosphonoacetone to acrylonitrile. The reactions, with exception of the first and the last, go slowly and have a very small thermal effect; for their completion they require the introduction into the reaction mixture of considerable amounts of catalyst and prolonged heating. With methyl acrylate we obtained two addition products – the methyl ester of γ-diethylphosphono-γ-acetobutyric acid and the dimethyl ester of γ-diethylphosphono-γ-acetopimelic acid. Both products are colorless, viscous liquids with a faint odor, readily soluble in organic solvents, partly soluble in water. In the remaining cases products of addition of phosphonoacetone to only one molecule of unsaturated compound were obtained. The constants, yields and analyses of the synthesized compounds are detailed in Table 2. Some of the preparations were saponified but we failed to obtain the corresponding acids in the crystalline form.

EXPERIMENTAL

Alkylation of phosphonoacetone. Synthesis of 2-diethylphosphonobutanone-3. The sodium derivative of phosphonoacetone was prepared in ethereal solution from 1.76 g metallic sodium and 15 g phosphonoacetone. The reaction was conducted with stirring and heating. After the whole of the sodium had reacted, 13 g methyl

* M.p. 75 – 76°.

iodide was added to the reaction mixture. Heating for 5 hours followed by fractionation gave 11.6 g 2-diethylphosphonobutanone-3.

B.p. 109–111° at 3 mm, n_D^{20} 1.4335, d_4^{20} 1.09[illegible], MR_D 50.29; calc. 50.02.

Found %: P 14.89, 14.51. $C_8H_{17}O_4P$. Calc. %: P 14.76.

Synthesis of 3-diethylphosphonopentanone-4. The potassium derivative of phosphonoacetone was prepared from 3.91 g metallic potassium and 19.6 g phosphonoacetone in ethereal solution. For completion of the reaction the mixture was heated on a water bath for 6 hours with stirring. 15.6 g methyl iodide was then run in, and heating and stirring were continued another 4 hours. Fractionation of the reaction mixture gave 14.8 g 3-diethylphosphonopentanone-4.

B.p. 128–129° at 11 mm, n_D^{20} 1.4370, d_4^{20} 1.0724, MR_D 54.28; Calc. 54.64.

Found %: P 14.44, 14.32. $C_9H_{19}O_4P$. Calc. %: P 13.97.

Procedure for adding phosphonoacetic ester and phosphonoacetone to unsaturated compounds. The reactions were performed with equimolar amounts of reactants in presence of sodium methoxide or ethoxide, as described in [6]. Depending upon the reactivity of the unsaturated compounds, the period of heating of the reaction mixtures varied between 0.5 and 3–4 hours.

TABLE 2.

Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Analysis for P (in %) found	Analysis for P (in %) calculated	Yield (in %)
$(C_2H_5O)_2PCHCH_3CH_2COOCH_3$ O $COCH_3$	160–162°(3)	1.4488	1.1347	66.16	65.53	11.31, 11.18	11.07	54
$(C_2H_5O)_2PC(CH_2CH_2COOCH_3)_2$ O $COCH_3$	188–192(1)	1.4582	–	–	–	8.37, 8.63	8.42	
$(C_2H_5O)_2PCHCHCH_2COOC_2H_5$ $COOC_2H_5$ O $COCH_3$	183–184(3)	1.4590	1.1725	85.35	85.65	8.56, 8.37	8.46	47.5
$(C_2H_5O)_2PCHC{=}CHCOOC_2H_5$ $COOC_2H_5$ O $COCH_3$	183(2)	1.4670	–	–	–	8.74, 8.54	8.52	10.0
$(C_2H_5O)_2PCCH_2CH_2CN$ C_2H_5 O $COCH_3$	185(5)	1.4577	1.1022	68.11	68.31	11.23, 11.18	11.27	70.5

SUMMARY

1. The addition was effected of phosphonoacetic ester to ester of acrylic and crotonic acids, as well as to nitriles of methacrylic and vinylacetic acids.

2. Phosphonoacetone was alkylated: 2-diethylphosphonobutanone-3 and 3-diethylphosphonopentanone-4 were synthesized.

3. It was shown that phosphonoacetone and its alkylated derivatives, in presence of alkoxides of alkali metals, add on to esters and nitriles of unsaturated carboxylic acids.

LITERATURE CITED

[1] A. N. Pudovik and N. M. Lebedeva, J. Gen. Chem., 22, 2128 (1952). (T.p. 2183)•

[2] A. N. Pudovik and N. M. Lebedeva, Proc. Acad. Sci. USSR, 90, 799 (1953).

[3] I. Michalski, B. Fischer, Roczniki Chemii, 26, 293 (1952).

[4] A. N. Pudovik and N. I. Plakatina, J. Gen. Chem., Supp. Vol. II, 831 (1953).

[5] A. I. Razumov and N. Petrov, Trans. Kazan Chem.-Tech. Inst., No. 10, 35 (1946).

[6] A. N. Pudovik, Prog. Chem., 22, 547 (1954).

Received February 20, 1955

Kazan Branch of the Academy of Sciences USSR

• T.p. = C. B. Translation pagination.

THE REACTIVITY OF ALKALI SALTS OF DIALKYL THIOPHOSPHORIC ACIDS

I. ALKYLATION REACTIONS

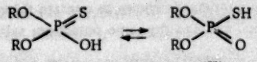
M. I. Kabachnik and T. A. Mastryukova

Metallic derivatives of tautomeric substances, such as keto-enols and lactim-lactams, are known to possess an extremely characteristic dual reactivity which is manifested in reactions of alkylation or acylation by the formation of O- or even C- (or N-) derivatives. According to A. N. Nesmeyanov [1] the dual reactivity in these and similar cases is associated not with tautomerism but with the presence of a system of conjugated double bonds in the molecules of these substances and with the resultant ability to enter not only into 1,2-reactions but also into 1,4-reactions (at the ends of the conjugated system of bonds).

Among the interesting tautomeric compounds of this type are thio acids containing the thiono-thiol grouping:

$$O{=}A{-}S{-}H \rightleftarrows H{-}O{-}A{=}S.$$

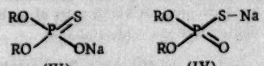
The atom A can be carbon in thiocarbonic acids, sulfur in thiosulfates, phosphorus in thiophosphates, etc. This type of thiono-thiol system of bonds is present also in dialkyl thiophosphates. Recently, in collaboration with S. T. Ioffe, we showed the occurrence of tautomeric equilibrium in these compounds [2]:



(I) (II)

We established that the equilibrium position depends markedly upon the nature of the solvent. Potentiometric investigation showed that an aqueous solution contains about 75% of the thiol isomer (II), while an alcohol solution contains 25%. Methylation with diazomethane of an ethereal solution of diethyl thiophosphoric acid (equilibrium mixture of isomers) led to formation of 80% of the derivative of form (II) and 20% of the isomeric derivative. Consequently, both the potentiometric investigation, with whose help the position of the tautomeric equilibrium was established, and the application of Arndt's diazomethane method indicate the presence of both forms in solutions of dialkyl thiophosphoric acids; hence it is perfectly natural to relate the dual reactivity of these acids (as in the cited reaction with diazomethane) to their tautomerism. In this connection the question of the reactivity of salts acquires great interest, in particular the reactivity toward alkylating and acylating agents.

In salts of dialkyl thiophosphoric acids, for which the structure (III) or (IV) may be advanced:



(III) (IV)

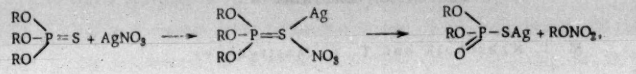
there is a $\sigma\pi$-conjugated system of bonds $Na{-}O{-}P{=}S$, or $Na{-}S{-}P{-}O$, or (with an ionic sturcture) the $p\pi$-conjugated system $\overset{\ominus}{O}{-}P{=}S$ or $\overset{\ominus}{S}{-}P{=}O$, which in themselves could be the cause of the development of dual reactivity.

If the structure of the salts corresponds to form (III) (which, as we shall show later, is more probable), then reactions of O-substitution will relate to the 1,2-type, and those of S-substitution to the 1,4-type of reactions.

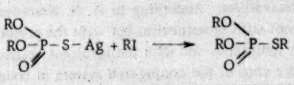
Literature data on the question of the structure and reactivity of salts of dialkylthiophosphoric acids

are conflicting. Assuming the possibility of existence of two isomeric salts of dialkyl monothiophosphoric acids, some authors have attempted to prepare them by various methods.

Pishchimuka [3] obtained the silver salts of dialkyl thiophosphoric acids by the action of silver nitrate on trialkyl thiophosphates:

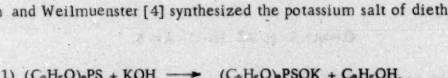


He assigned to them, in correspondence with the formation reaction, a thiol sturcture. He naturally proposed the same sturcture (IV) for the sodium salts, since the silver salts obtained from them were identical with those mentioned above. On alkylation of these salts with alkyl halides, Pishchimuka obtained trialkyl thiophosphates:



which, in his opinion, confirmed the structure of the salts as thiol derivatives.

Mastin, Norman and Weilmuenster [4] synthesized the potassium salt of diethyl thiophosphoric acid by three routes:



In the first two methods they started from compounds known to contain thiono sulfur; in the third method the sulfur was thiol. In all three cases they obtained one and the same potassium salt with m.p. 196–197°.

In a study of the alkylation of the diethyl thiophosphates of potassium, sodium and silver, A. E. Arbuzov and O. M. Shapshinskaya [5] attributed a thiono structure to these salts (III).

Schrader, in his patent specification on the synthesis of Isosystox [6], postulates the tautomerism of the salts of dialkyl thiophosphoric acids (III) $\rightleftarrows$ (IV) on the basis of their dual reactivity.

Since salts of dialkyl thiophosphoric acids, whatever their structure, can react both with migration of a reaction center and without it, we must recognize the impossibility of drawing any specific conclusion about the structure of the starting salts and still less about their tautomerism on the basis of the sturcture of the products of alkylation. In this case physical data are the most reliable, and primarily spectral investigations.

Gore [7] studied the infarared spectra of numerous thiophosphorus-organic compounds and found that the spectrum of the solid potassium salt of diethyl thiophosphoric acid is lacking in the characteristic, usually very intense band in the 1200–1300 cm^{-1} region corresponding to the P=O bond. On this basis he assigned a thiono structure to this salt. In the light of these more trustworthy data and taking into account the higher electro negativity of oxygen in comparison with sulfur, we must assume that alkali salts of dialkyl thiophosphoric acids most probably possess the thion structure (III) (with strongly ionized O–Me linkage).

It was recalled above that Pishchimuka alkylated the silver salts of dialkyl thiophosphoric acids with alkyl halides and obtained trialkyl thiophosphates whose structure could be established with difficulty. Hoegberg and Cassady [8] reported that alkylation of the potassium salt of diethyl thiophosphoric acid gave thiol derivatives. They wrote that they arrived at this conclusion on the basis of a study of the infrared spectra although they did not give further details.

Arbuzov and Shapshinskaya [5] assigned a thiono structure to the products of alkylation of diethylthiophosphoric salts with ethyl iodide and bromide, on the basis of a comparison of the physical constants of triethylthiophosphate, obtained by alkylation, with the constants of the triethyl thionophosphate described by Pishchimuka.

Schrader [6] alkylated the sodium salts of dialkyl thiophosphoric acids with chloroalkyl-alkyl sulfides

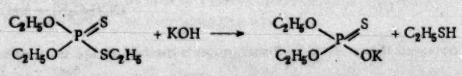
$ClCH_2CH_2SR$ and assigned a thiol structure to the products, in particular to the isomer of the known insecticide "Systox" $(C_2H_5O)_2PO(SCH_2CH_2SC_2H_5)$. Spectral investigations [9] (infrared spectra) later confirmed the structure of "Systox" as the thiono isomer and that of "Isosystox" as the thiol isomer.

We undertook a special investigation of the problem in view of the conflicting data of different authors for the direction of the alkylation of alkali salts of dialkyl thiophosphoric acid, a subject of extreme interest from the standpoint of the study of the reactivity of salts of tautomeric substances.

In the first place we had to convince ourselves of the identity of the starting salts employed by various authors in alkylation reactions. We synthesized the potassium salts of diethyl thiophosphoric acid by the method of Arbuzov [10] and Foss [11]–by addition of sulfur to potassium diethyl thiophosphite in ether-alcohol solution:

$$(C_2H_5O)_2POK + S \longrightarrow (C_2H_5O)_2PSOK,$$

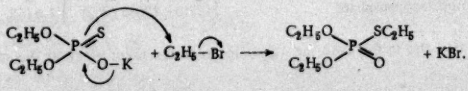
as well as by the methods of Pishchimuka [3]–saponification of triethyl dithiophosphate with alcohol solution of potassium hydroxide:



and by saponification of triethyl thiophosphate with alcoholic solution of potassium hydroxide, which was also used by Mastin et al [4] (equation 1). In all cases we obtained one and the same potassium salt of diethyl thiophosphoric acid with m.p. 196–197° in exact agreement with the literature data [4,12]. Consequently all five methods of synthesis lead to one and the same salt which was investigated by Gore [7]. Consequently all the authors who studied the alkylation of this salt were dealing with one and the same substance. There is no doubt that we can say the same about the corresponding sodium salt.

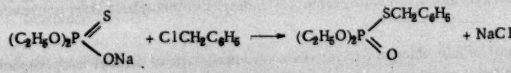
We studied the reaction of alkylation of the potassium and sodium salts of diethyl thiophosphoric acid with ethyl bromide and benzyl chloride in alcoholic solution with heating on a water bath for 4 hours. Reaction with ethyl bromide gave an 80% yield of triethyl thiophosphate with constants closely agreeing with those cited by Pishchimuka for the thiol isomer. For comparison we synthesized the thiol and thion isomers by the methods of Pishchimuka which gave products of established structure. The constants of the substances obtained are set forth in Table 1.

The data of Table 1 leave no doubt whatever that alkylation with ethyl bromide of the potassium salt of diethyl thiophosphoric acid gives triethyl thiophosphate. Since the salt has the thion structure, we are forced to the conclusion that its alkylation with ethyl bromide goes with migration of the reaction center:



In the alkylation of the sodium, potassium and silver salts of diethyl thiophosphoric acid with ethyl iodide and ethyl bromide, Arbuzov and Shapshinskaya obtained one and the same substance with b.p. 118° at 20 mm and n_D ranging from 1.4520 to 1.4530. We must therefore conclude that their experiments likewise gave the thiol isomer and that the nature of the metal of the salt and of the halogen of the alkyl halide does not influence (as far as shown by the examples studied) the direction of the alkylation, which proceeds in all cases at the sulfur.

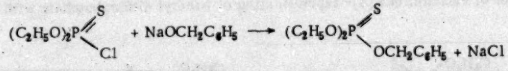
Benzylation of sodium diethyl thiophosphate with benzyl chloride likewise led to the thiol isomer in 55% yield:



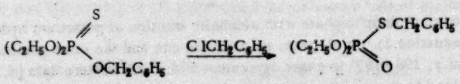
For proof of its sturcture we synthesized diethylbenzylthionophosphate from diethylchlorothionophosphate and sodium benzylate:

TABLE 1.

Substance	Boiling point at 20 mm	n_D^{20}	d_4^{20}	d_4^0
1) $(C_2H_5O)_2PO(SC_2H_5)$				
a) Prepared by us by alkylation	122.5–123°	1.4578	1.1067	1.1254
b) Synthesized by us by Pishchimuka's method	121.5–122.5	1.4580	1.1063	1.1254
a) Described by Pishchimuka	122	–	–	1.1245
2) $(C_2H_5O)_2PS$				
a) Prepared by us by Pischimuka's method	105–105.5	1.4500	1.0768	1.0945
b) Described by Pishchimuka	106	–	–	1.0944



and we isomerized the obtained thiono ester by Pishchimuka's method to the thiol ester by heating with benzyl chloride:



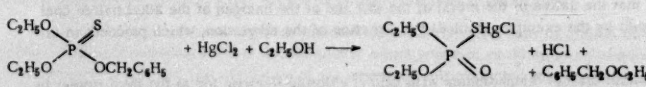
As we see from Table 2, the constants of the product of benzylation of sodium diethyl thiophosphate agree with the constants of the thiol isomer and differ markedly from those of the thion isomer.

TABLE 2.

Substance	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}
1) $(C_2H_5O)_2PO(SCH_2C_6H_5)$			
a) Prepared by alkylation	137.5–138° (2.5)	1.5258	1.1569
b) Obtained by isomerization of the thiono isomer	140–141 (3)	1.5275	1.1589
2) $(C_2H_5O)_2PS(OCH_2C_6H_5)$			
Obtained from chlorothionophosphate	122.5–123.5 (2.5)	1.5152	1.1301

Consequently also in this case the alkylation reaction takes place at the sulfur, i.e. with migration of the reaction center.

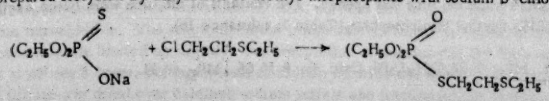
We also found that the isomers differ in their behavior toward an alcoholic solution of mercuric chloride. Diethylbenzyl thionophosphate reacts with alcoholic mercuric chloride with liberation of one equivalent of hydrochloric acid which may be quantitatively determined. The reaction is evidently as follows:



Unlike diethylbenzyl thionophosphate, diethyl-S-benzyl thiolphosphate does not react with alcoholic mercuric chloride.

Thus the action of simple halogen derivatives upon alkali salts of diethyl thiophosphoric acid leads to S-alkylation. We considered it of interest to clarify the mode of substitution in more complicated cases. For this purpose we repeated the work [6] on the synthesis of Isosystox since the patent does not mention any constants that would permit an objective comparison of the properties of the prepared isomer with those of Systox.

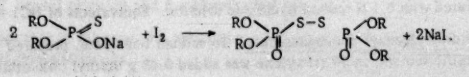
We prepared Isosystox by alkylation of diethyl thiophosphate with sodium β-chlorodiethyl sulfide:



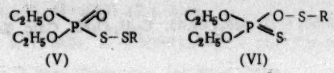
In this way was obtained an 87% yield of a substance with b.p. 127–128° at 1.5 mm, n_D^{20} 1.4982, d_4^{20} 1.1388. The only data reported for Isosystox are b.p. 134° at 1 mm[13] and 132–133° at 1 mm [6].

In regard to Systox, its boiling point is close to that of the isomer; but the remaining constants are very different [14]: b.p. 134° at 2 mm, n_D^{20} 1.4875, d_4^{20} 1.1183. Such a difference in constants is perfectly normal; as a rule, thiol isomers boil higher and have a higher refractive index and specific gravity. Here again, therefore, the alkylation of sodium diethyl thiophosphate takes place at the sulfur, i.e. with migration of the reaction center.

Reactions other than alkylation of salts of dialkyl thiophosphoric acids also lead to formation of S-isomers. Foss [11] found that oxidation of salts of dialkyl thiophosphates with iodine in an alkaline medium or electrochemically led to formation of the corresponding disulfides:



We found that reaction of the sodium salt of diethyl thiophosphoric acid with alkylsulfenechlorides results in formation of disulfides for which only one structure (V) is possible:



(V) (VI)

Formation in this reaction of mixed anhydrides of sulfoxylic acids (VI) is altogether improbable.

EXPERIMENTAL

Preparation of potassium diethyl thiophosphate. Preparation was effected: 1) according to [4], yield 54%, after recrystallization from dry methanol 37%, m.p. 197°; 2) by Pishchimuka's method [3], yield 55%, after recrystallization 32%, m.p. 196–197°; and 3) by the method of Arbuzov [10] and Foss [11], yield 68%. Mixed samples melted at 196–197°.

Sodium diethyl thiophosphate. Prepared by the method of Foss [11]. Yield 95%, and after recrystallization from chloroform and ether 60%, m.p. 198°.

Alkylation of potassium diethyl thiophosphate with ethyl bromide. To a solution of 10.3 g potassium diethyl thiophosphate in 40 ml dry alcohol was added 16.3 g ethyl bromide. The addition resulted in a slight turbidity, and the precipitate of potassium bromide only started to come down on heating. The reaction mixture was heated on a water bath at 70–80° for 4 hours. After cooling, the precipitate of potassium bromide was filtered off; it weighed 5.57 g (the theoretical amount is 5.95 g). The filtrate was fractionated in vacuum. Two distillations gave 7.9 g (80%) of triethyl thiophosphate (Table 1, substance 1a).

Found%: P 15.69, 15.44. MR_D 48.85. $C_6H_{15}O_3PS$. Calc. %: P 15.66. MR_D 49.11.

Preparation of triethyl thionophosphate. Triethyl thionophosphate was prepared by Pishchimuka's method [3] (Table 1, substance 2a).

Found %: C 35.94, 36.25; H 7.25, 7.24. MR_D 49.42. $C_6H_{15}O_3PS$. Calc. %: C 36.36; H 7.58. MR_D 49.40.

Isomerization of triethyl thionophosphate to triethyl thiolphosphate. 9.8 g triethyl thionophosphate was heated in a sealed tube with 16.5 g ethyl bromide at 160–170° for 3 hours. The liquid remained nearly

colorless. No pressure was apparent when the tube was opened. The contents of the tube were twice fractionated in vacuum. Yield 6.1 g (61%) triethyl thiolphosphate (Table 1, substance 1b).

Found %: P 15.53, 15.67. MR_D 48.84. $C_6H_{15}O_3PS$. Calc. %: P 15.66. MR_D 49.11.

Alkylation of sodium diethyl thiophosphate with benzyl chloride. To a solution of 9.6 g sodium diethyl thiophosphate in 40 ml dry alcohol was added 18.97 g benzyl chloride. The reaction mixture was heated on a water bath at 70–80° for 4 hours. On cooling, the precipitate of sodium chloride was filtered off; it weighed 2.7 g (theoretical 2.9 g). The filtrate was dried over calcined sodium sulfate and twice fractionated in vacuum to give 7.2 g (55%) of diethyl-S-benzyl thiolphosphate (Table 2, substance 1a).

Found %: C 50.55, 50.49; H 6.62, 6.76; P 11.91, 12.12. MR_D 69.06. $C_{11}H_{17}O_3PS$. Calc. %: C 50.75; H 6.58; P 11.91. MR_D 68.74.

Action of alcoholic mercuric chloride upon diethyl-S-benzyl thiolphosphate. To a weighed amount of the compound was added 10 ml 20% solution of mercuric chloride in anhydrous alcohol. Only slight turbidity appeared on standing. After 30 minutes methyl orange was added, and the evolved minute amount of hydrochloric acid was titrated with 0.1 N sodium hydroxide solution. Equivalents of HCl found: 0.08, 0.08.

Preparation of diethylbenzyl thionophosphate. To sodium benzylate, prepared from 5.4 g benzyl alcohol and 1.15 g metallic sodium, in 50 ml xylene was added 9.43 g diethyl chlorothiophosphate dropwise with stirring. Slight heat was developed. The reaction mixture was heated on a water bath at 60° for an hour. The precipitate of sodium chloride was then filtered off, and the filtrate was dried over calcined sodium sulfate and fractionated in vacuum. Yield 8.3 g (63%) diethylbenzyl thionophosphate (Table 2, substance 2).

Found %: C 50.48, 50.43; H 6.50, 6.73. MR_D 69.48. $C_{11}H_{17}O_3PS$. Calc. %: C 50.75; H 6.58. MR_D 69.03.

Action of alcoholic mercuric chloride upon diethylbenzyl thionophosphate. To a weighed amount of the substance was added 10 ml 20% solution of mercuric chloride in anhydrous alcohol. A precipitate at once began to come down. After 20 minutes the hydrochloric acid liberated during the reaction was titrated with sodium hydroxide in presence of methyl orange. Equivalents of HCl found: 1.02, 1.02.

Isomerization of diethylbenzyl thionophosphate to diethyl S-benzylthiolphosphate. 6.5 g diethylbenzyl thiolphosphate was heated in a sealed tube with 12.65 g benzyl chloride at 140–145° for 2¼ hours. No pressure was found when the tube was opened. The contents of the tube had darkened. On the walls was a white amorphous precipitate. Two fractionations in vacuum gave 1.3 g (20%) diethyl-S-benzyl thiolphosphate (Table 2, substance 1b).

Found %: P 12.16, 12.08. MR_D 69.11. $C_{11}H_{17}O_3PS$. Calc. %: P 11.91. MR_D 68.74.

Action of alcoholic mercuric chloride upon diethyl-S-benzyl thiolphosphate. To a weighed amount of the substance was added 10 ml 20% solution of mercuric chloride in anhydrous alcohol. Only a faint turbidity appeared on standing. After 30 minutes, methyl orange was added and the minute amount of liberated hydrochloric acid was titrated with 0.1 N sodium hydroxide solution. Equivalents of HCl found: 0.07, 0.06.

Alkylation of sodium diethyl thiophosphate with β-chlorodiethyl sulfide. To 38.4 g sodium diethyl thiophosphate and 50 ml dry alcohol was added 24.4 g β-chlorodiethyl sulfide. The mixture was heated on a water bath at 65–75°. A precipitate started to come down in 20 minutes from the start of heating and quickly settled to the bottom. Heating at 80–85° was continued for another 3 hours. The precipitate of sodium chloride was then filtered; weighed 11.5 g (theoretical 11.7 g). The filtrate was dried over calcined sodium sulfate and fractionated in vacuum to give 45.0 g (87%) diethyl-S-(β-ethylmercaptoethyl)-thiolphosphate (Isosystox, constants as above).

Found %: C 37.24, 37.31; H 7.01, 7.53. MR_D 66.52. $C_8H_{19}O_3PS_2$. Calc. %: C 37.19; H 7.41. MR_D 66.34.

Preparation of diethyl-S-(butylthio)-thiolphosphate. To 10.3 g sodium diethyl thiophosphate and 10 ml carbon tetrachloride was added in small portions and with stirring 6.5 g butylsulfene chloride in 7 ml carbon tetrachloride. The reaction started immediately, the sulfene chloride quickly decolorized, and the reaction mixture heated up slightly. For completion of the reaction the flask contents were heated on a water bath at 40° for 3 hours; the precipitate of sodium chloride was then filtered; weighed 3.5 g (theoretical 2.9 g). The filtrate was dried over calcined sodium sulfate and fractionated in vacuum to give 6.8 g (52%) diethyl-S--(butylthio)-thiol phosphate with b.p. 132–134° at 4 mm, n_D^{20} 1.4885, d_4^{20} 1.1248.

Found %: P 11.64, 11.76. $C_8H_{19}O_3PS_2$. Calc. %: P 12.01.

Preparation of diethyl-S-(ethylthio)-thiolphosphate. Prepared as above, from 13.44 g sodium diethyl thiophosphate and 9.0 g ethylsulfene chloride. Yield 1.4 g (9%). B.p. 82–85° at 3.5 mm, n_D^{20} 1.4721, d_4^{20} 1.1224.

Found %: P 13.69, 13.39. $C_6H_{15}O_3PS_2$. Calc. %: P 13.49.

SUMMARY

1. A study was made of the alkylation of alkali salts of diethyl thiophosphoric acid with various alkyl halides: ethyl bromide, benzyl chloride and β-chlorodiethyl sulfide.

2. It was shown that in all cases the alkylation takes place at the sulfur with formation of the corresponding diethyl-S-alkyl thiolphosphates.

LITERATURE CITED

[1] A. N. Nesmeyanov, Sci. Memoirs Moscow State Univ., 132, No. 5 (1950); A. N. Nesmeyanov and M. I. Kabachnik, J. Gen. Chem., 25, 41 (1955). (T.p. 37)•

[2] M. I. Kabachnik, S. T. Ioffe, T. A. Mastryukova, J. Gen. Chem., 25, 684 (1955). (T.p. 653)•

[3] P. S. Pishchimuka, J. Russ. Chem. Soc., 44, 1406 (1912).

[4] W. Mastin, G. R. Norman, E. A. Weilmuenster, J. Am. Chem. Soc., 67, 1662 (1945).

[5] A. E. Arbuzov and O. M. Shapshinskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., 152, 845.

[6] German Pat. 830509; C. A., 47, 1727 (1953).

[7] R. C. Gore, Disc. Farad. Soc., 1950, 138.

[8] E. I. Hoegberg, J. T. Cassaday, J. Am. Chem. Soc., 73, 557 (1951).

[9] A. Henglein, G. Schrader, R. Muhlmann, Z. anal. Chem., 141, 276 (1954).

[10] A. E. Arbuzov, Abstracts 6th Mendeleev Congress, part II, 124 (1932).

[11] O. Foss, Acta Chem. Scand., 1, 12 (1947).

[12] A. E. Arbuzov and O. M. Shapshinskaya, Trans. Kazan Inst. Chem. Tech., No. 16, 3 (1952).

[13] German Pat. 830508; Chem. Zentr., 1953, 1391.

[14] U. S. Pat. 2571989; Chem. Zentr., 1953, 2182; N. N. Malnikov, Prog. Chem., 22, 273 (1953).

Received January 16, 1955

Institute of Organoelement Compounds Academy of Sciences USSR

• T.p. = C. B. Translation pagination.

THE POLYMERIZATION OF ALLYL ESTERS OF ALKYLARYL PHOSPHONIC ACIDS

Gilm Kamai and V. A. Kukhtin

In the preceding communications [1,2] we described experiments on the polymerization of various unsaturated esters of phosphonocarboxylic and α-ketophosphonic acids.

In a recently published paper by Toy and Cooper [3] the polymerization of a large group of new allyl esters of phosphonic acids was described. In reporting the preparation of diallyl phosphite, the authors of this paper do not mention that this compound had already been synthesized and studied by one of us in collaboration with E. I. Shugurova in 1949 [4]. We had prepared and studied in 1952 [1] another compound described by them – the allyl ester of benzyl phosphonic acid. Toy and Cooper were clearly unacquainted with our researches.

In the present communication we describe the syntheses of some new allyl esters of phosphonic acids and the results of a study of their susceptibility to polymerization. The starting allyl esters of aryl phosphinous acids, obtained by the action of allyl alcohol upon the corresponding dichloroaryl phosphines in presence of pyridine, partly isomerized during fractional distillation and formed esters of allylaryl phosphonic acids in a similar manner to the methyl ester of phenyl phospohinous acid [5].

A series of allyl esters of alkylaryl phosphonic acids was synthesized by the action of various alkyl halides on the allyl esters of phenyl phosphinous and p-chlorophenyl phosphinous acids. Their constants are given in the table.

A study of the polymerization tendency of the aryl phosphinous acids showed that they had no tendency at all to polymerize. Probably the unsaturated character of the trivalent phosphorus in these compounds hinders their polymerization. On prolonged heating with benzoyl peroxide they only undergo an insignificant change of color. Of the esters of alkylaryl phosphonic acids that we prepared, only the allyl esters of allylphenyl phosphonic and allyl-p-chlorophenyl phosphonic acids form low-molecular polymers. Heating with benzoyl peroxide gives transparent, colorless, sticky resins with a degree of polymerization of n = 2–3. The polymers are readily soluble in many organic solvents (benzene, acetone, dichloroethane).

EXPERIMENTAL

Preparation of the allyl ester of phenyl phosphinous acid

In a three-necked flask, fitted with stirrer, dropping funnel and reflux condenser, were placed 40 g allyl alcohol, 54 g pyridine and 300 ml anhydrous ether. 60 g phosphenyl chloride was added through the dropping funnel with intensive stirring and cooling of the reaction mass. At the end of the reaction, the pyridine hydrochloride was separated on a vacuum filter and the solvent was distilled off; the reaction products were then fractionated in vacuum. Two products were isolated.

1st fraction. B.p. 116–117° (3 mm). Yield 32 g (42.6%). The substance reacts with cuprous chloride with considerable heat development; it is therefore a derivative of trivalent phosphorus.

d_4^0 1.0620, d_4^{20} 1.0443, n_D^{20} 1.5240, MR_D 65.06. $C_{12}H_{15}O_2P$. Calc. 64.50.

Found %: C 64.48; H 6.99. $C_{12}H_{15}O_2P$. Calc. %: C 64.82; H 6.79.

2nd fraction. B.p. 131–132° (2 mm). Yield 10 g (13.3%). It does not react with cuprous chloride and is consequently a derivative of pentavalent phosphorus.

d_4^0 1.0971, n_D^{20} 1.5280.

Found %: C 64.37; H 7.03. $C_{12}H_{15}O_2P$. Calc. %: C 64.82; H 6.79.

Action of allyl bromide on the allyl ester of phenyl phosphinous acid. 29 g allyl ester of phenyl phosphinous acid and 10 g allyl bromide were refluxed in a small flask on a glycerol bath. At a bath temperature of 80° the temperature in the flask rose to 95–100° and remained at this level after removal of the bath for 20 minutes. For completion of the reaction the flask was heated another 2 hours at 100–110°. The allyl bromide was then distilled off and the residue vacuum fractionated to give 20 g allyl ester of allylphenyl phosphonic acid.

B.p. 131–132° (2 mm), d_0^0 1.0980, n_D^{20} 1.5280.

The allyl esters of methylphenyl phosphonic and ethylphenyl phosphonic acids were prepared in like fashion.

Preparation of allyl ester of p-chlorophenyl phosphinous acid

In a three-necked flask fitted with dropping funnel, stirrer and reflux condenser, were placed 19 g allyl alcohol, 26 g pyridine and 200 ml anhydrous ether as solvent. Addition of 35 g p-chlorophenyl dichlorophosphine was effected through the dropping funnel with snow cooling and intensive stirring. Vacuum fractionation was carried out after separation of the pyridine hydrochloride and distillation of the solvent. Two fractions were collected.

1st fraction. B.p. 126–127° (2 mm). Yield 24 g (56.5%); reacts with cuprous chloride to form a crystalline compound.

d_0^0 1.1685, d_0^{20} 1.1490, n_D^{20} 1.5376, MR_D 69.79. $C_{12}H_{14}O_2PCl$. Calc. 69.37.

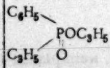
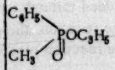
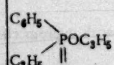
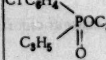
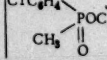
Found %: C 55.86; H 5.32. $C_{12}H_{14}O_2PCl$. Calc. %: C 56.16; H 5.49.

2nd fraction. B.p. 148° (2 mm). Yield 6 g. Does not react with cuprous chloride.

d_0^0 1.2060, d_0^{20} 1.1203, n_D^{20} 1.5338, MR_D 66.99. $C_{12}H_{14}O_2PCl$. Calc. 67.17.

Found %: C 55.78; H 5.89. $C_{12}H_{14}O_2PCl$. Calc. %: C 56.16; H 5.49.

TABLE

Preparation No.	Formula	Boiling point (pressure in mm)	n_D^{20}	d_0^{20}	Content (in %) Found	Content (in %) Calculated
1	$C_6H_5P(OC_3H_5)_2$	116–117° (3)	1.5240	1.0443	C 64.48 H 6.99	C 64.82 H 6.79
2		131–132 (2)	1.5280	1.0971	C 64.37 H 7.03	C 64.82 H 6.79
3		112–113 (1)	1.5208	1.1110	P 15.70	P 15.79
4		124–125 (3)	1.5155	1.0854	C 62.67 H 7.21	C 62.87 H 7.20
5	$ClC_6H_4P(OC_3H_5)_2$	126–127 (3)	1.5376	1.1490	C 55.86 H 5.32	C 56.16 H 5.49
6		148–149 (2)	1.5338	1.1203	C 55.82 H 5.76	C 56.16 H 5.49
7		129–130 (2)	1.5308	1.1960	C 51.84 H 5.31	C 52.08 H 5.25

Rearrangement of the p-chlorophenyl phosphinous ester with allyl bromide and methyl iodide was performed in the same way as the above-described rearrangement of the phenyl phosphinous ester.

The constants of the synthesized compounds are given in the table.

Polymerization

The polymerization technique was the same as in [2]; Allyl esters of alkylaryl phosphonic acids were polymerized at 70° with addition of 1% benzoyl peroxide. Under these conditions the ester of phenylallyl phosphonic acid polymerizes in 60 hours, the p-chlorophenylallyl phosphonic ester after 100 hours. On further heating the degree of polymerization does not change. The remaining esters did not polymerize even after 200 hours heating.

SUMMARY

Allyl esters of the following acids were synthesized: phenyl phosphinous, p-chlorophenyl phosphinous, phenylmethyl phosphonic, phenylethyl phosphonic, phenylallyl phosphonic, p-chlorophenylallyl phosphonic, p-chlorophenylmethyl phosphonic. The susceptibility to polymerization of the esters was studied.

LITERATURE CITED

[1] Gilm Kamai and V. A. Kukhtin, Trans. Kazan Chem.-Tech. Inst., 16, 29 (1952).

[2] Gilm Kamai and V. A. Kukhtin, J. Gen. Chem., 24, 1855 (1954). (T.p1819)•

[3] A. O. F. Toy, R. S. Cooper, J. Am. Chem. Soc., 76, 2191 (1954).

[4] Gilm Kamai and E. I. Shugurova, J. Gen. Chem., 21, 658 (1951). (T.p. 727)•

[5] A. E. Arbuzov, J. Gen. Chem., 4, 898 (1934).

Received November 22, 1954

Kazan S. M. Kirov Institute of Chemical Technology

• T.p. = C. B. Translation pagination.

SYNTHETIC ANESTHETICS

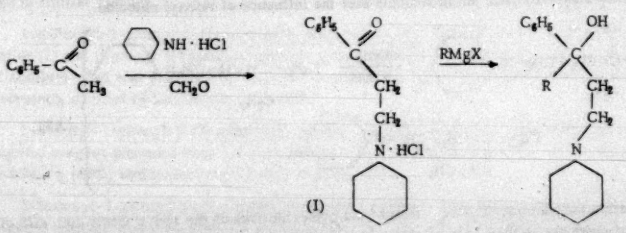
II. ESTERS OF 1-ALKYL-1-PHENYL-3-(N-PIPERIDYL)-PROPAN-1-OLS

I. N. Nazarov and E. M. Cherkasova

The subject of our systematic investigations comprises esters of diverse alkyl-aromatic aminoalcohols with the objective of finding new highly active anesthetic substances. In the preceding communication [1] we described the synthesis of a series of esters of 1-alkyl-1-phenyl-3-dialkylaminopropan-1-ols containing dimethylamino and diethylamino groups as the amino residue. Some members of this series were found to be strong anesthetics approximating in activity to pontocaine* but 4–5 times less toxic (phenoxyacetate of 1-ethyl-1-phenyl-3-dimethylaminopropan-1-ol). It appeared of interest to synthesize the structural analogs of these compounds containing the piperidine group as the nitrogen residue.

The literature contains many examples illustrating the high anesthetic and spasmolytic activity of various compounds containing a piperidine ring in the β-position and belonging to the classes of amides [2], aminoketones [3], aminoalcohols [4], etc. However, esters of alkyl-aromatic aminoalcohols containing a piperidine residue have scarcely been investigated, and descriptions have appeared of only a few members possessing a fortuitous character.

The starting substance for synthesis of the compounds in question was the readily available acetophenone which was transformed by the Mannich reaction into β-N-piperidylpropiophenone (I); the latter was converted into various aminoalcohols by the Grignard reaction:



(III) R = CH_3; (IV) R = C_2H_5;
(V) R = n-C_3H_7; (VI) R = n-C_4H_9;
(VII) R = iso-C_5H_{11}.

Some of these aminoalcohols were recently obtained in 15–13% yield by the action of Grignard reagents upon aminoketones [4a]. In the Grignard reactions we used not the free aminoketones but their hydrochlorides and secured 78–96% yields of the aminoalcohols. A comparison of the yields of tertiary aminoalcohols by the action of Grignard reagents upon aminoketones and their hydrochlorides is given in the table.

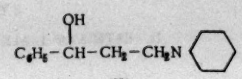
In addition the secondary aminoalcohol (II) has been obtained in 83% yield by the catalytic reduction of β-piperidylpropiophenone over palladium catalyst [5].

The aminoalcohols were subsequently transformed into various esters (acetates, propionates, butyrates, benzoates, cinnamates and hydrocinnamates) by the action of the chlorides or anhydrides of the acids.

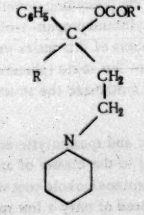
* Translator's note: = 2-dimethylaminoethyl p-butylaminobenzoate hydrochloride.

TABLE

Amino-alcohols	Yields (in %)	
	from amino-ketones [4a]	from hydro-chlorides
(III)	14.6	78
(IV)	22.8	96
(V)	35.6	87
(VI)	25.9	88
(VII)	34.7	80

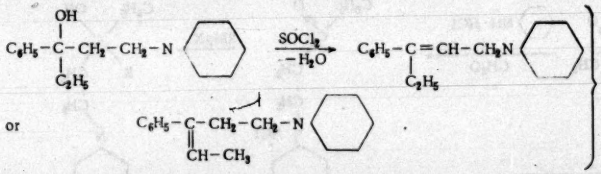


(II)



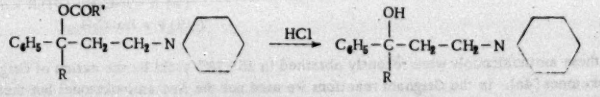
(VIII) R = H, R' = $CH_2OC_6H_5$; (IX) R = CH_3, R' = C_6H_5; (X) R = CH_3, R' = CH = CHC_6H_5; (XI) R = CH_3, R' = $CH_2OC_6H_5$; (XII) R = C_2H_5, R' = CH_3; (XIII) R = R' = C_2H_5; (XIV) R = C_2H_5, R' = C_3H_7; (XV) R = C_2H_5; R' = C_6H_5; (XVI) R = C_2H_5, R' = $CH_2OC_6H_5$; (XVII) R = = C_2H_5, R' = CH= CHC_6H_5; (XVIII) R = n $-C_3H_7$, R' = C_6H_5; (XIX) R = n $-C_4H_9$, R' = C_6H_5; (XX) R = iso$-C_5H_{11}$, R' = C_6H_5.

In this reaction we encountered a number of difficulties associated with the dehydration of the amino-alcohols and with cleavage of the esters under the action of acids or hydrogen chloride. Particulary prone to dehydration are tertiary alkyl-aromatic aminoalcohols uner the influence of thionyl chloride:



(XXI)

The preparation for pharmacological tests of the hydrochlorides of the above esters met with difficulty in a number of cases due to their ease of cleavage in presence of hydrogen chloride:



For this reason we were unable to prepare the hydrochlorides of certain esters (XVIII, XIX, XX). On passing dry hydrogen chloride into an ethereal or chloroform solution of these esters, only the hydrochlorides of the corresponding aminoalcohols were obtained.

Some of the compounds synthesized were tested at the S. Ordzhonikidze Scientific Research Institute of Pharmaceutical Chemistry (laboratory of Prof. M.D. Mashkovsky) as anesthetics and spasmolytics. The most active of these compounds as anesthetics were the hydrochlorides of the benzoate of 1-ethyl-1-phenyl-3-(N--piperidyl)-propan-1-ol (XV) and of the phenoxyacetate of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XI), although both of these preparations were inferior to pontocaine in activity. All the esters in question possess elements of spasmolytic acitivity. It must be admitted that in tests on isolated organs (ear and intestines of the rabbit) the benzoate of (XV) did not differ appreciably from pontocaine and exhibited little activity in

experiments on animals.

EXPERIMENTAL*

1-Phenyl-3-(N-piperidyl)-propan-1-ol (II). 5 g β-N-piperidylpropiophenone (I) (m.p. 188–189°), prepared by the Mannich reaction [5], was hydrogenated in presence of palladium on calcium carbonate (5% Pd) in 125 ml distilled water. Hydrogenation was performed for 16 hours, after which period addition was made in small portions (about 0.1 g) of 0.75 g catalyst. The hydrogen absorption was 455 ml (440 ml theoretical). The catalyst was filtered off, the water was driven off in vacuum, and the residue was treated with ammonia. The product was extracted with ether (200 ml) and dried with sodium sulfate. Removal of the ether left 3.6 g (83.4%) 1-phenyl-3-(N-piperidyl)-propan-1-ol (II) with m.p. 66–67° [5].

1-Methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (III). Methyl magnesium iodide was prepared by the usual procedure from 5.27 g magnesium, 31.2 g methyl iodide and 105 ml absolute ether. To the prepared solution, with energetic stirring and cooling to 10–12°, was added 15.9 g β-N-piperidylpropiophenone hydrochloride (I) in small portions. The reaction mass was stirred 2 hours at room temperature and left overnight. The next day the mixture was heated on a water bath for about 2 hours, and was hydrolyzed with hydrochloric acid (1:1) while cooling with ice. The aqueous layer was treated with ammonia until it had an alkaline reaction to litmus; the separated base was thoroughly extracted with ether, dried with sodium sulfate and fractionated in vacuum to give 11.4 g (78%) aminoalcohol (III) with b.p. 135–139° at 2.5 mm [4].

1-Ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (IV). To a solution of methyl magnesium bromide, prepared from 5.6 g magnesium, 25.3 g ethyl bromide and 80 ml absolute ether, was added portionwise 18.2 g β-N-piperidylpropiophenone hydrochloride (I) with stirring and cooling to −10°. The next day the mixture was heated 2 hours at 35°, cooled and acidified with hydrochloric acid (1:1) until the precipitate had completely dissolved. The neutral products were twice extracted with ether and the acidic aqueous layer saturated with solid caustic alkali. The separated oil was extracted many times with ether. The ethereal extract was dried with sodium sulfate. Removal of the ether left 19 g crystalline aminoalcohol. The product was recrystallized from benzene. Yield 17.1 g (96%) aminoalcohol (IV) with m.p. 79–81°. Other tertiary aminoalcohols were prepared in similar fashion.

1-n-Propyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (V). From 25.3 g β-piperidylpropiophenone hydrochloride (I) and n-propyl magnesium bromide prepared from 8.4 g magnesium, 46 g n-propyl bromide in 150 ml absolute ether was obtained by the usual treatment 22.7 g (87%) aminoalcohol (V) with m.p. 89–90.5° (from acetone), m.p. of hydrochloride 195–196°.

1-n-Butyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (VI). From 25.3 g aminoketone hydrochloride (I) and Grignard reagent prepared from 7.8 g magnesium, 45 g n-butyl bromide and 150 ml absolute ether was obtained 24.4 g (88%) aminoalcohol (VI) with m.p. 51–52°.

1-Isoamyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (VII). From 25.3 g aminoketone hydrochloride (I) and Grignard reagent, prepared from 7.8 g magnesium and 50 g isoamyl bromide in 150 ml absolute ether, was obtained 23.2 g (80%) aminoalcohol (VII) with m.p. 56–57°.

Phenoxyacetate of 1-phenyl-3-(N-piperidyl)-propan-1-ol (VIII). To a solution of 3.42 g aminoalcohol (II) in 4 ml dry benzene was gradually added, with ice-cooling, 5.88 g phenoxyacetyl chloride. Heating-up and momentary crystallization of the entire mass were observed. The mixture was heated on a boiling water bath for 3 hours, and then 30 ml water and 2–3 ml hydrochloric acid (1:1) were added. The neutral products were extracted. The aqueous layer was treated with saturated sodium carbonate solution; the product was extracted with ether and the ether solution dried with sodium sulfate before fractionation in vacuum. There were obtained 0.9 g original aminoalcohol (II) and 3.20 g (78.9%) phenoxyacetate of 1-phenyl-3-(N-piperidyl)-propan-1-ol (VIII) with b.p. 186.5–188.5° at 1.5 mm.

Found %: N 4.15, 3.81. $C_{22}H_{27}O_3N$. Calc. %: N 3.96.

The hydrochloride of the phenoxyacetate of 1-phenyl-3-(N-piperidyl)-propan-1-ol (VIII) melted at

* Students I. Nikolaeva and A. Podorolskaya participated in the experimental work.

168.5–170° (from acetone – chloroform mixture).

Found %: C 68.02, 67.46; H 7.68, 7.22; N 3.76, 3.59. $C_{22}H_{28}O_3NCl$. Calc. %: C 67.74; H 7.18; N 3.59.

Benzoate of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (IX). To a solution of 2.33 g amino-alcohol (III) in anhydrous acetone was added 1.82 g benzoyl chloride (freshly distilled) dropwise at 0° with stirring. White crystals came down after a few minutes. The next day the precipitate was filtered and thoroughly washed with anhydrous acetone. Weight of precipitate 2.95 g, 156.5–159°. Three recrystallizations from acetone gave 1.87 g (50%) hydrochloride of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (IX) with m.p. 180–182°. (The author who first prepared it reports m.p. 175–177° [6]).

Found %: N 3.74, 4.03. $C_{23}H_{28}O_2NCl$. Calc. %: N 3.74.

Cinnamate of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (X). To a solution of 2.33 g amino-alcohol (III) in 5 ml benzene was added 0.24 g fine magnesium turnings, with cooling with ice water, a solution of 2 g cinnamyl chloride (m.p. 34–35°)in 5 ml benzene was slowly run in. The precipitate was triturated in absolute ether and then twice recrystallized from acetone – chloroform – alcohol mixture and boiled with a little acetone. The crystals (1.9 g) were dissolved in acetone (with addition of a few drops anhydrous alcohol) and boiled 2 hours with active carbon on a water bath. The solution was filtered and cooled for complete separation of the crystals. The hydrochloride of the cinnamate of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (X) was obtained with m.p. 188–189.5°. Weight 1.45 g (36%).

Found %: C 71.68, 71.52; H 7.04, 7.21; N 3.56, 3.69. $C_{24}H_{30}O_2NCl$. Calc. %: C 72.09; H 7.50, N 3.50.

Phenoxyacetate of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XI). To a solution of 1.85 g amino-alcohol (III) in 6 ml absolute ether was slowly added a solution of 2.04 g phenoxyacetyl chloride in 4 ml absolute ether. Slight heat was developed and the hydrochloride was quickly precipitated. After a few days the crystalline mass was filtered, triturated in absolute ether and recrystallized several times from anhydrous acetone. The poorly acetone-soluble hydrochloride of the original aminoalcohol (0.4 g) first separated; it did not give a depression in admixture with an authentic specimen. The solvent was distilled off from the mother liquor and the residual crystals thoroughly triturated in absolute ether and then recrystallized (2–3 times) from acetone.

1.1 g of the phenoxyacetate of 1-methyl-1-phenyl-3-(N-piperidyl)-propan-1-ol hydrochloride was obtained with m.p. 139.5–141° (yield 43.8%).

Found %: C 68.79, 67.77; H 7.13, 7.31; N 3.85, 3.79. $C_{23}H_{30}O_3NCl$. Calc. %: C 68.40; H 7.43; N 3.47.

Acetate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XII). A mixture of 3 g aminoalcohol (IV), 3.72 g acetic anhydride and 15 ml pyridine was heated 2 hours at 120°. The pyridine and excess of acetic anhydride were then distilled off in the vacuum of a water jet pump. The residual viscous oil was dissolved in water and acidified with 2 ml hydrochloric acid (1:1); the neutral products were extracted and the acidic aqueous layer saturated with sodium carbonate. The oil that separated was extracted several times with ether (150 ml). The ethereal extracts were dried with sodium sulfate, the ether was distilled off, and the residue distilled in vacuum to give 2.87 g acetate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XII) with b.p. 138.5–139.5° at 1.5 mm; it was at once converted to the hydrochloride with m.p. 136–138° (from acetone). Yield 81.6%.

Found %: C 66.00, 66.01; H 8.14, 8.39; N 4.25, 4.38. $C_{18}H_{28}O_2NCl$. Calc. %: C 66.35; H 8.61; N 4.29.

Propionate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XIII). A mixture of 3 g aminoalcohol (IV), 4.75 g propionic anhydride and 15 ml dry pyridine was heated 2 hours at 130°. The pyridine and excess propionic anhydride were then taken off in vacuum. Further procedure was as in the preceding experiment. Two distillations gave 1.42 g original alcohol (IV) and 1.5 g of the base of the propionate (XIII) with b.p. 141–142° at 1 mm. Yield approximately 41%.

The base was at once converted to propionate of 1-phenyl-1-ethyl-3-(N-piperidyl)-propan-1-ol

hydrochloride (XIII), m.p. 158.5–159° (from acetone).

Found %: N 4.07, 4.08. $C_{19}H_{30}O_2NCl$. Calc. %: N 4.12.

Butyrate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XIV). To a solution of 5 g aminoalcohol (IV) in 6 ml dry benzene was gradually added (cooling) 8.74 g freshly distilled butyl chloride (b.p. 90–91°). Heat was developed. The mass solidified on standing and was heated 1½ hours at 120°, after which the excess of butyryl chloride was distilled off in vacuum. Further procedure was as described above for the preparation of the acetate (XII). Two distillations gave 1.36 g original aminoalcohol (IV) and 1.37 g butyrate of 1-ethyl--1-phenyl-3-(N-piperidyl)-propan-1-ol (XIV) with b.p. 156–158° at 2 mm. Yield about 30%.

Found %: C 75.36, 75.24; H 9.78, 9.85. $C_{20}H_{31}O_2N$. Calc. %: C 75.6; H 9.78.

Benzoate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XV). To a solution of 5 g aminoalcohol (IV) in 10 ml dry benzene was gradually added (cooling with ice water) 10.15 g benzoyl chloride in 11 ml dry benzene. Heat was developed and crystals came down after 10–15 minutes. The mixture was then heated 2 hours at 120°. The benzene was driven off in vacuum and the residue worked up as in the case of the acetate (XII).

Distillation gave 2 g original aminoalcohol (IV) and 2.6 g benzoate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XV) with b.p. 186–187° at 1.5 mm. Yield 37%.

Found %: C 78.06, 78.53; H 7.99, 8.21; N 4.26, 4.35. $C_{23}H_{29}O_2N$. Calc. %: C 78.5; H 8.25; N 4.01.

The hydrochloride of the benzoate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol melts at 155.5–157° (from acetone).

Found %: N 3.78, 3.89. $C_{23}H_{30}O_2NCl$. Calc. %: N 3.61.

Phenoxyacetate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XVI). To a solution of 3.24 g aminoalcohol (IV) in 5 ml dry benzene was gradually added (ice cooling) 8.95 g phenoxyacetyl chloride in 4 ml dry benzene. Slight heat was developed. After 5 hours heating at 130–140° the entire mass crystallized. It was worked up as in the preceding experiment. There was obtained 1.05 g phenoxyacetate of 1-ethyl-1--phenyl-3-(N-piperidyl)-propan-1-ol (XVI) with b.p. 148–150° at 0.4 mm.

Found %: N 3.81, 3.37. $C_{24}H_{31}O_3N$. Calc. %: N 3.67.

The hydrochloride of the phenoxyacetate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XVI) melts at 156–157° (from acetone).

Found %: N 3.35, 3.58. $C_{24}H_{32}O_3NCl$. Calc. %: N 3.35.

Cinnamate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XVII). To a solution of 2.47 g alcohol (IV) in 4 ml dry benzene was added 0.24 g magnesium, and in the cold a solution of 2.5 g cinnamyl chloride in 3.5 ml dry benzene was run in. A yellowish precipitate gradually came down. The next day the filtered precipitate was washed with absolute ether and recrystallized from acetone; the crystals were dissolved in a mixture of acetone and alcohol and boiled with active carbon on a water bath. A second recrystallization from acetone gave 1.1 g (26.7%) of the hydrochloride of the cinnamate of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XVII) with m.p. 170–172°.

Found %: C 72.20, 72.24; H 6.96, 7.48; N 3.48, 3.25. $C_{25}H_{32}O_2NCl$. Calc. %: C 72.55; H 7.73; N 3.38.

Benzoate of 1-n-propyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XVIII). 0.345 g sodium was dispersed at 100–110° in 15 ml dry dioxane. After cooling, the aminoalcohol (V) was added and the reaction mass heated with stirring for 4 hours. The unreacted sodium was removed, the reaction mixture was cooled with ice, and dropwise addition was made of 2.42 g freshly distilled benzoyl chloride. The mixture was heated 2 hours, and

then 50 ml water and 2 g sodium carbonate were added. The resultant oil was extracted with ether (250 ml) and dried with sodium sulfate. Vacuum distillation gave the base (XVIII) in the form of a viscous oil which slowly crystallized. M.p. 93.5–94°. Weight 3.45 g (63%).

Found %: C 79.14, 79.34; H 8.74, 8.64; N 3.88, 3.97. $C_{24}H_{31}O_2N$. Calc. %: C 78.90; H 8.49; N 3.83.

0.1 g base of the benzoate (XVIII) was dissolved in chloroform and a stream of hydrogen chloride was passed through the cooled solution until acid to congo. A few drops of absolute ether were added. The precipitate was filtered and recrystallized from acetone. The hydrochloride of the original aminoalcohol (V) was obtained; it did not give a depression with an authentic specimen.

Found %: N 4.58, 4.63. $C_{17}H_{28}ONCl$. Calc. %: N 4.7.

Benzoate of 1-n-butyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XIX). a) Preparation in pyridine medium. A reaction mixture containing 0.75 g aminoalcohol (VI), 0.75 g benzoic anhydride (prepared from benzoic acid and acetic anhydride [7]) and 0.75 ml pyridine was heated 5 hours at 140–155°. The mass acquired a dark-brown color. After many recrystallizations from acetone, 0.19 g (18.4%) of the benzoate of 1-n-butyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XIX) was obtained with m.p. 109–111°.

Found %: N 3.71, 3.70. $C_{25}H_{33}O_2N$. Calc. %: N 3.69.

b) Preparation via the sodium alcoholate. 0.09 g sodium was dispersed in 5 ml dry benzene. After cooling, 1 g aminoalcohol (VI) was added and the reaction mixture heared 4 hours. The next day the unreacted sodium was separated, 0.6 g benzoyl chloride was added, and the mixture heated 2½ hours. After cooling, the mass was decomposed with water (30 ml) and saturated with sodium carbonate solution. The separated oil was extracted several times with ether (100 ml) and dried with sodium sulfate. Vacuum distillation gave a heavy, viscous oil of the benzoate of 1-n-butyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XIX). The oil gradually crystallized after washing with ether. M.p. 110–112°. Weight 0.75 g (54.7%).

Found %: C 78.92, 79.30; H 8.81, 8.64; N 3.59, 3.81. $C_{25}H_{33}O_2N$. Calc. %: C 79.15; H 8.7; N 3.69.

0.15 g base of the benzoate (XIX) was dissolved in absolute ether and a solution of hydrogen chloride in absolute ether was added. The amount of hydrogen chloride introduced was in slight excess over the calculated amount. The oil containing precipitate melted at 168–194°. Two recrystallizations from acetone gave the hydrochloride of the original alcohol (VI) which melted at 214–216° and did not give a depression with an authetic specimen

Found %: N 4.26, 4.43. $C_{18}H_{30}ONCl$. Calc. %: N 4.5.

Benozate of 1-isoamyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XX): 0.23 g sodium was dispersed in 10 ml dry dioxane. Addition was then made in small portions of 2.89 g aminoalcohol (VII). The mass was heated 4 hours. The unreacted sodium was removed and dropwise addition was made (cooling) of 1.54 g benzoyl chloride. The reaction mass was heated another 2½ hours. Further treatment was as in the preceding experiment. There was obtained 2.22 g (56.5%) of the benzoate of 1-isoamyl-1-phenyl-3-(N-piperidyl)-propan-1-ol (XX) which after washing with isooctane melted at 85.5–87°.

Found %: N 3.18, 3.66. $C_{26}H_{35}O_2N$. Calc. %: N 3.56.

The base (XX) was dissolved in a mixture of ether and chloroform and dry hydrogen chloride was passed through until acid to congo. A few drops of absolute ether were added. The resultant precipitate of the hydrochloride of the original alcohol (VII) melted before recrystallization at 232–234° and after recrystallization from acetone at 238–240°.

Found %: N 4.32, 4.38. $C_{19}H_{32}ONCl$. Calc. %: N 4.3.

Dehydration of 1-ethyl-1-phenyl-3-(N-piperidyl)-propan-1-ol. To a solution of 5 g alcohol (IV)

in 6 ml dry benzene was gradually added 12.1 g thionyl chloride. After 5 hours boiling the thionyl chloride and benzene were distilled off from the reaction mass. The precipitate was dissolved in water, the neutral products were extracted with ether, and the acidic layer saturated with sodium carbonate. The oil was extracted with ether (200 ml). After drying over sodium sulfate and removal of the ether, the residue was distilled to give 3.35 g (72.5%) product of dehydration (XXI) with b.p. 117–119° at 1 mm.

Found %: C 83.47, 83.60; H 9.89, 9.81; N 6.22, 6.40. $C_{16}H_{23}N$. Calc. %: C 83.5; H 10.05; N 6.11.

The hydrochloride of the dehydration product (XXI) melts at 198–200° (from acetone).

Found %: N 5.02, 5.33. $C_{16}H_{24}NCl$. Calc. %: N 5.27.

SUMMARY

Reaction with Grignard reagents of the hydrochlorides of β-(N-piperidyl)-propiophenones gave 78–96% yields of 1-alkyl-1-phenyl-3-(N-piperidyl)-propan-1-ols (III-VII) which were transformed into various esters (VIII-XX) with the objective of pharmacological investigation.

The esterification of 1-alkyl-1-phenyl-3-(N-piperidyl)-propan-1-ols goes with considerably greater difficulty than in the case of their analogs containing a dimethylamino residue.

LITERATURE CITED

[1] I. N. Nazarov and E. M. Cherkasova, J. Gen. Chem., 25, 1536 (1955). (T.p. 1485)*

[2] Sommers, Freifelder et. al., J. Am. Chem. Soc., 75,57 (1953).

[3] Profft, Chem. Tech., 5, 15 (1953).

[4] a) Denton et. al., J. Am. Chem. Soc., 71, 2048, 2050, 2053, 2054 (1949); b) Doshay, Constable et. al., J. Am. Med. Assoc., 140, 1317; Corbin, J. Am. Med. Assoc., 141, 377 (1949).

[5] Mannich, Lammering, Ber., 55, 3510 (1922).

[6] Adamson et. al., J. Chem. Soc., 1951, 56.

[7] Synth. Org. Prep., 1,96 (1949).

Received December 13, 1954

M. V. Lomonosov Institute of Fine Chemical Technology, Moscow

* T.p. = C. B. Translation pagination.

THE SULFONATION OF UNSATURATED COMPOUNDS

II. SULFONATION OF ACETYLENIC HYDROCARBONS. THE MECHANISM OF SULFONATION WITH DIOXANESULFOTRIOXIDE

A. V. Dombrovsky and G. M. Prilutsky

One of us [1] has described the sulfonation of acrolein and crotonaldehyde with dioxanesulfotrioxide. In the present paper we report the results of the action of this agent upon some hydrocarbons containing a triple bond: acetylene, 1-hexyne and phenylacetylene.

Very few instances are known of the hydrogen atoms at the triple bond of acetylenic hydrocarbons and their derivatives being replaced by inorganic radicals and functional groups. Thus, the direct nitration and sulfonation of hexadecyne-1 with concentrated nitric and sulfuric acids [2] gave respectively $C_{14}H_{29}C\equiv C-NO_2$ and $C_{14}H_{29}C\equiv C-SO_3H$. Treatment of phenylacetylene with concentrated sulfuric acid caused carbonization of the hydrocarbon [3]. Rondestvedt [4] failed to isolate phenylacetylenesulfonic acid in appreciable amounts on sulfonation with dioxanesulfotrioxide in the cold.

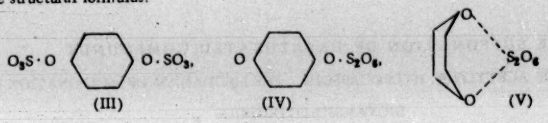
We carried out the sulfonation of acetylene by passing the gas into a suspension of dioxanesulfotrioxide in dichloroethane at room temperature. The reaction gave two salts of sulfonic acids, whose composition and structure corresponded to the formulas $CH_2(SO_3H)-CHO$ (I) and $HC\equiv C-SO_3H$ (II), in yields of 57 and 35% respectively reckoned on the reacted acetylene. Acetaldehydesulfonic acid and its salts have been described in the literature [5], but the barium salt of acetylenemonosulfonic acid (II) is here obtained for the first time. It is poorly soluble in water so that on evaporation of the solution it is easily separated from the barium salt of acid (I). The potassium salt of acetylenesulfonic acid has good solubility in water; the solutions decolorize bromine water and potassium permanganate and the substance undergoes complete breakdown with formation of CO_2 and potassium sulfate. Acetylenesulfonic acid is isolated in the free state by the action of dilute sulfuric acid on its barium salt. During concentration of the solution by evaporation on a bath or in vacuum, however, the acid decomposes with formation of a resinous substance and sulfuric acid.

Sulfonation of hexyne-1 under similar conditions gave a barium salt corresponding to the monosulfonic acid $C_6H_9-SO_3H$. Solutions of the salt gave the usual reactions at the multiple bond.

Phenylacetylene reacted with dioxanesulfotrioxide at room temperature to give a nearly quantitative yield of acetophenonemonosulfonic acid; the barium and potassium salts of the latter are nicely crystallizing substances. The structure of the sulfonic acid was proved by oxidation of a solution of the potassium salts with potassium permanganate and by hydrolysis in a weakly acidic medium. In the former case benzoic acid was identified among the reaction products; hydrolysis gave acetophenone, identified as the semicarbazone.

Although numerous papers have appeared on the utilization of dioxanesulfotrioxide, this complex has been inadequately studied. We observed that addition of the first portions of dioxane to a solution of sulfur trioxide in dichloroethane caused the appearance of white crystals which gradually went into solution as more dioxane was added in excess. We separated the crystals and analyzed them after freeing from solvent. Their composition corresponded to the formula $C_4H_8O_2 \cdot S_2O_6$, in agreement with the data of Ya. F. Mezhenny and E. A. Martynenko [6]; the latter found by the cryoscopic method that sulfur trioxide has a double molecular weight in highly dilute solutions in dioxane. The same authors established that solutions of sulfur trioxide in dioxane are completely non-conductive. In the absence of moisture, crystalline dioxanesulfotrioxide can be stored for several weeks without appreciable decomposition; it is stable up to 75° but further rise of temperature causes violent breakdown with copious evolution of sulfur dioxide. Water quickly decomposes dioxanesulfotrioxide to dioxane and sulfuric acid. Crystalline dioxanesulfortrioxide reacts violently and with considerable heat development with pyridine to form pyridinesulfotrioxide. It does not dissolve in dichloroethane, benzene and ligroine, but has good solubility in dioxane.

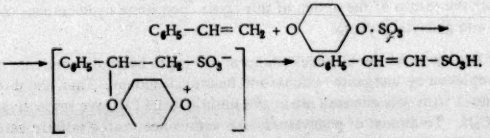
Concerning the structure of the complex, it can, in our opinion, be represented by one of the following three structural formulas:



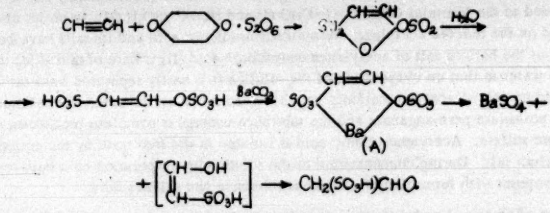
(III) (IV) (V)

If dioxanesulfotrioxide is compared with complexes of dioxane with bromine, iodine, aluminum bromide, etc. [7-9], then the two last formulas must be rejected. But if we take account of the small dipole moment (approximately 0.4 D) of dioxane, the structure represented by (V) is more probable.

The following reaction scheme was advanced in 1948 in a paper devoted to the mechanism of sulfonation with dioxanesulfotrioxide, using styrene as test material [10]:

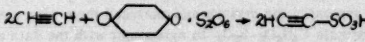


We regard the mechanism of sulfonation of acetylenic hydrocarbons and the formation of sulfo compounds containing a carbonyl group as involving the addition of sulfur trioxide at the triple bond with formation of a compound of the type of carbyl sulfate which on subsequent treatment undergoes hydrolysis; the barium salt is later transformed. This mechanism can be represented thus in the case of acetylene:



Although salt (A) readily hydrolyzes, especially when heated, it was nevertheless possible, by careful concentration at room temperature in vacuum-desiccator, to isolate it in the form of crystals. On heating aqueous solutions of this salt, the medium becomes acidic, barium sulfate comes down, and sulfoacetaldehyde can be detected in the solution after neutralization. In a similar fashion we explain the formation of acetophenonesulfonic acid on sulfonation of phenylacetylene.

Concerning monoacetylene sulfonic acid (II), its formation in our opinion is due to a concurrent reaction of direct substitution of the extremely mobile hydrogen atom of the acetylene molecule as a result of nucleophilic exchange:



This mechanism may possibly apply to the sulfonation with dioxanesulfotrioxide in the α-position of saturated aldehydes, ketones and carboxylic acids of the aliphatic series [5,11].

EXPERIMENTAL

Sulfonation of acetylene. Dioxanesulfotrioxide was prepared by the published method [1] from 40 g sulfur trioxide, dissolved in 160 ml dichloroethane, and 44 ml dioxane. In a three-necked flask fitted with mechanical stirrer and mercury seal, was placed a freshly prepared suspension of dioxane sulfotrioxide, and

acetylene was passed into it from a gasholder with continuous stirring and external heating to 30–40°. The acetylene was purified with chromic acid mixture and 2 N potassium hydroxide and dried with calcium chloride. The speed of introduction was 5–6 bubbles per second. The unreacted acetylene flowed into a second gasholder. The gasholders were periodically switched round. After absorption of 5.3 liters acetylene, the contents of the flask were carefully treated with an aqueous suspension of barium carbonate until the reaction was neutral, and then filtered. A part of the filtrate was left to evaporate at room temperature in a vacuum-desiccator. The remaining (greater) part of the filtrate was evaporated on a water bath. When about half of the solvent had gone off, the solution was again neutralized by addition of barium carbonate and filtered; the filtrate was again evaporated. Crystals of salt (II) gradually started to come down. The crystals (14 g) were recrystallized from water, washed with ether and dried.

Found %: Ba 39.50. $C_4H_2O_6S_2Ba$. Calc. %: Ba 39.52.

The potassium salt, prepared from the barium salt by double decomposition with potassium sulfate, also corresponded to the monosulfonic acid.

Found %: K 27.28. C_2HO_5SK. Calc. %: K 27.12.

Aqueous solutions of acetylenesulfonic acid decolorized bromine water and potassium permanganate; at the same time $SO_4^{=}$ ions were detected in the solution and CO_2 came off.

A fraction of barium salt of (I), isolated on evaporation of the mother liquor after separation of the salt of the monoacetylenesulfonic acid (II), was recrystallized from water and dried in a vacuum-desiccator over phosphorus pentoxide:

Found %: Ba 36.02. $C_4H_6O_8S_2Ba$. Calc. %: Ba 35.81.

Solutions of the salt did not decolorize potassium permanganate and did not react with bromine water, but they gave a black precipitate with ammoniacal solution of silver nitrate and reduced Fehling solution; a color was not formed, however, with fuchsinesulfurous acid.

By careful evaporation at room temperature in a vacuum-desiccator, a salt was obtained which was separated from a small amount of the salt of the monoacetylenesulfonic acid (II) which had first come down; after washing with anhydrous alcohol and ether it corresponded to the composition $C_2H_2O_7S_2Ba$.

Found %: Ba 41.51. $C_2H_2O_7S_2Ba$. Calc. %: Ba 40.46.

Boiling of a solution of the salt led to precipitation of $BaSO_4$ and the medium became acidic. Neutralization of the filtrate with barium carbonate resulted in separation of the barium salt of sulfoacetaldehyde.

Sulfonation of hexyne-1. From 3.2 g hydrocarbon (b.p. 71–71.5°, n_D^{20} 1.3968), sulfonated with 10 g dioxanesulfotrioxide at 30–40°, followed by the usual treatment with barium carbonate and water, was obtained 5.3 g (59%) barium salt corresponding to the monosulfonic acid.

Found %: Ba 30.06. $C_{12}H_{18}O_6S_2Ba$. Calc. %: Ba 30.15.

Sulfonation of phenylacetylene. 6.3 g phenylacetylene (b.p. 143–144°, n_D^{20} 1.5442) in 30 ml dichloroethane was sulfonated at room temperature with dioxanesulfotrioxide prepared from 9 g sulfur trioxide and 10.5 ml dioxane. After the mixture had been kept 45 minutes, it was treated in the usual manner with an aqueous suspension of barium carbonate until neutral. The filtrate gave a conspicuous reaction for the $SO_4^{=}$ ion. Evaporation gave 16.7 g light-yellow, finely crystalline barium salt.

Found %: Ba 25.51. $C_{16}H_{14}O_8S_2Ba$. Calc. %: Ba 25.64.

The potassium salt likewise corresponded to the monosulfonic acid of acetophenone.

Found %: K 16.96. $C_8H_7O_4SK$. Calc. %: K 16.41.

Oxidation of the Ba salt of acetophenonesulfonic acid. To a weakly acid solution of 3 g salt in 5 ml water was added 4.7 g finely pulverized $KMnO_4$ in small portions. Toward the end the reaction mixture was heated on a water bath until decolorized. Evaporation and acidification of the filtrate led to separation of crystals of benzoic acid (m.p. 121.5°).

Hydrolysis of the Ba salt was effected by heating 2 g of the substance in water faintly acidified with hydrochloric acid. The acetophenone was extracted with ether and identified from the melting point of its semicarbazone (197°).

Complex of dioxane with sulfur trioxide. To a solution of 40 g sulfur trioxide in 200 ml dichloroethane was added in small portions, with stirring and cooling (0–3°), a solution of 22 g anhydrous dioxane in 22 ml dichloroethane. The precipitated white crystals were collected on a glass filter and freed from solvents (these operations were conducted with exclusions of atomspheric moisture). The crystals had m.p. 69–70° (determined in a Zhukov apparatus). Further rise of temperature resulted in decomposition accompanied by explosion.

A weighed amount of the substance was carefully brought into 100 ml water, and the sulfuric acid formed was titrated with sodium hydroxide.

Found %: SO_3 64.31. $C_4H_8O_2 \cdot S_2O_6$. Calc. %: SO_3 64.50.

The composition of the product does not change when dissolved in dioxane and the solution is carefully evaporated.

To 2.3 g dioxanesulfotrioxide (with good external cooling) was added 1.5 ml dry pyridine. The reaction mixture was washed several times with iced water. The resultant crystals (3 g) were dried between sheets of filter paper (m.p. 175°).

SUMMARY

1. It was shown that dioxanesulfotrioxide reacts with acetylenic hydrocarbons; acetylene gives a mixture of sulfoacetaldehyde and monoacetylenesulfonic acid; phenylacetylene is sulfonated to acetophenonesulfonic acid. Salts of the sulfonic acids were prepared and described.

2. Theories of the mechanism of sulfonation of hydrocarbons containing a triple bond are advanced.

3. It was established that dioxanesulfotrioxide has the composition $C_4H_8O_2 \cdot S_2O_6$ in the solid state. Some properties of crystalline dioxanesulfotrioxide were studied.

LITERATURE CITED

[1] A. V. Dombrovsky, J. Gen. Chem., 22, 2136 (1952). (T.p. 2191)*

[2] F. Krafft, H. Heizmann, Ber., 33, 3856 (1900).

[3] C. Friedel, M. Bolson, Ber., 14, 364 (1881).

[4] C. S. Rondestvedt, J. Am. Chem. Soc., 76, 1926 (1954).

[5] A. P. Terentyev and L. A. Yanovskaya, Proc. Acad. Sci. USSR, 75, 235 (1950); A. P. Terentyev, A. N. Kost, A. M. Yurkevich and E. E. Khaskina, J. Gen. Chem., 23, 746 (1953). (T.p. 779)*

[6] Ya. F. Mezhenny and E. A. Martynenko, J. Gen. Chem., 18, 2042 (1948).

[7] A. E. Favorsky, J. Russ. Chem. Soc., 38, 741 (1906).

[8] I. A. Sheka and K. F. Karlysheva, J. Gen. Chem., 21, 8313 (1951). (T.p. 915)*

[9] J. A. Crowder, C. A., 40, 6092 (1946).

[10] F. G. Bordwell, C. S. Rondestvedt, J. Am. Chem. Soc., 70, 2429 (1948).

[11] A. P. Terentyev, L. A. Yanovskaya, A. M. Berlin and E. A. Borisov, Bull. (Vestnik) Moscow State Univ., No. 6, 117 (1953); W. E. Truce, C. E. Olson, J. Am. Chem. Soc., 75, 1651 (1953).

Received January 4, 1955

Chernovits State University

* T.p. = C. B. Translation pagination.

REDUCTION WITH FORMIC ACID AND ITS DERIVATIVES

II. THE REDUCTION OF QUINOLINE

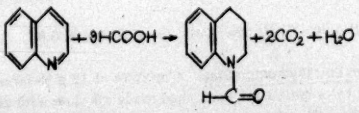
A. N. Kost and L. G. Yudin

Lukes [1] found that pyridine is not reduced when heated with formic acid and potassium formate whereas pyridine metholbromide gives N-methylpiperidine under these conditions. According to Mayo [2], under drastic conditions (autoclave, 175–200°) pyridine forms N-methylpiperidine on reaction with formaldehyde (or methanol); in this case, however, it is suggested that pyridine itself is not reduced but the N-methylpyridinium ion.

Our experiments have shown that quinoline, in contrast with pyridine, is reduced by reaction with formic acid (better in presence of sodium formate) to give N-formyl-tetrahydroquinoline in yields of up to 85% (see table).

The reaction of quinoline with 85% formic acid goes very sluggishly on boiling. Introduction of catalytic amounts of oxalic and sulfuric acids suppresses the reaction, but additions of iridium, nickel or aluminosilicate catalyst cause accelerated decomposition of the formic acid although they do not shorten the duration of the reaction and do not increase the yield. A closer study of the influence of nickel showed that it even slightly lowers the yield of hydrogenated product when the reaction is conducted in presence of sodium formate. Introduction of sodium formate (optimum 5 moles per mole quinoline) raises the boiling point of the mixture and slightly alters the acidity of the medium with the result that already after 18–20 hours heating without a catalyst good yields of N-formyltetrahydroquinoline are obtained.

According to the equation



1 mole quinoline requires 3 moles formic acid, but it was found that 5 moles acid are needed since decomposition of formic acid takes place by a complex process: both CO_2 and CO are evolved in the course of the reaction. Replacement of 85% formic acid by anhydrous acid raises the yield of N-formyltetrahydroquinoline by a few percent.

TABLE

Reduction of quinoline by formic acid

Molar ratio			Duration	Temperature	Catalyst	Yield (%)
C_9H_7N	HCOOH	HCOONa	(in hours)			
1	3.7	–	70	120°	–	53
1	3.7	–	12.5	120	Houdry	25
1	3.7	–	12.5	120	Ni	20
1	3.7	–	12.5	120	Ir	25
1	5	–	20	120	Ni	36
1	3.7	1.5	12.5	140	–	60
1	3.7•	1.5	12.5	140	–	67
1	5	3.3	35	140	Ni	70
1	5•	5	20	140	Ni	71.2
1	5	5	20	140	–	82.5
1	5•	5	21	140	–	85.5

• Anhydrous formic acid

Consequently the reduction of quinoline by a mixture of formic acid and sodium formate goes smoothly, and substantially without secondary reactions. The unreacted quinoline is completely recovered from the reaction mixture in all experiments.

Reaction of quinoline with formamide likewise gives N-formyltetrahydroquinoline, but in this case there is serious resinification. Satisfactory results (55% yield) were only secured by adding formic acid to the formamide. It is interesting to note that although Leuckardt hydramination of ketones is accelerated by addition of Ni [3], in the present case Ni evidently accelerates not the principal but the secondary reaction, since resinification is much more serious in presence of nickel. N-formyltetrahydroquinoline could be separated from the reaction mass in overall yield of about 80–85%. In addition, resinous colored substances were obtained whose structure was not established.

Reduction of quinoline evidently proceeds through the stage of formation of the quinolinium ion, while in reduction with formamide the process is complicated by condensation at the formyl group with splitting-off of water.

EXPERIMENTAL

Reduction of quinoline with formic acid in presence of sodium formate. A mixture of 12.9 g (0.1 mole) quinoline, 23 g (0.5 mole) anhydrous formic acid and 34 g (0.5 mole) anhydrous sodium formate was refluxed in a flask for 21 hours with periodical stirring. The reaction mass was then diluted with water and a 30% sodium hydroxide solution was added until the reaction was strongly alkaline. The oil that separated was extracted with ether, the ethereal extract was dried with sodium sulfate, the ether was driven off on a water bath, and the residue was distilled in vacuum to give 2 g quinoline with b.p. 84–90° (at 4–4.5 mm) and 14.3 g N-formyltetrahydroquinoline with b.p. 136–147° (at 4–4.5 mm).

Redistillation of the second fraction gave 13.6 g (85%) N-formyltetrahydroquinoline with b.p. 145–147° (4 mm). A viscous, syrupy liquid crystallizing on cooling. Readily soluble in ethyl alcohol, ether, benzene, acetone, dichloroethane and isopentane, poorly soluble in dilute hydrochloric acid and ligronine. N-formyltetrahydroquinoline was recrystallized by dissolution in boiling anhydrous ether, cooling to –10 to –15°, and precipitating with ligroine. After standing for 48 hours in a vacuum-desiccator, crystals with m.p. 38.5° were obtained.

Found %: C 74.11; H 6.90. $C_{10}H_{11}ON$. Calc. %: C 74.50; H 6.87.

Hydrolysis of N-formyltetrahydroquinoline. A mixture of 12 g N-formyltetrahydroquinoline and 50 g concentrated hydrochloric acid was boiled one hour, then made alkaline with concentrated sodium hydroxide solution and extracted with ether; the ether extract was dried with fused caustic alkali, the ether was driven off on a water bath and the residue distilled in vacuum to give 8.6 g (94.4%) 1, 2, 3, 4-tetrahydroquinoline.

B.p. 95–97° (at 3–4 mm), n_D^{20} 1.5951, d_4^{20} 1.0599, MR_D 42.74; Calc. 42.19. Hydrochloride, m.p. 180°; N-phenylcarbamide derivative, m.p. 98° (from ether); benzoyl derivative, m.p. 74°; picrate, m.p. 140°.

A mixed melting test with the picrate of tetrahydroquinoline (m.p. 141–142°), obtained by reduction of quinoline with zinc in hydrochloric acid, did not give a depression.

Literature data: b.p. 250–251° [4,6], n_D^{20} 1.5958, d_4^{20} 1.0608; hydrochloride m.p. 180.6–181.4°; picrate, m.p. 140.5–141.5° [4]; benzoyl derivative, m.p. 75° [5].

Reduction of quinoline with formamide. A mixture of 12.9 g (0.1 mole) quinoline, 26 g (0.55 mole) formamide and 2.3 g anhydrous formic acid was refluxed in a flask for 6 hours. The formamide mixed with formic acid was introduced in lots of 7.1 g every 1½ hours. The mixture was heated another 2½ hours (temperature of mixture 185–190°), 250 ml water and concentrated sodium hydroxide solution were added until strongly alkaline, and the mass left for 3 hours with shaking (for complete decomposition of the formamide). It was then extracted with ether and the ether removed on a water bath. To the viscous, dark residue was added 10 g anhydrous formic acid; it was then refluxed in a flask for 20 minutes (for complete formylation of the free tetrahydroquinoline). After making alkaline, ether extraction and distillation, there were obtained 3 g quinoline with b.p. 86–93° (at 6 mm) and 0.7 g N-formyltetrahydroquinoline with b.p. 138–149° (at 6 mm). Redistillation gave 8.9g (55%) N-formyltetrahydroquinoline with b.p. 143–145° (at 3 mm), crystallizing on cooling.

After purification as described above, the m.p. was 37–38°. A mixed melting test with the substance got by reduction of quinoline with formic acid did not give a depression.

On conducting the reduction in the absence of formic acid (6 hours, 190°), the yield is only 37%. Prolongation of the heating period to 12 hours does not increase the yield. With addition of skeletal nickel the yield is 45–50%. Replacement of formic acid by sodium formate leads to serious resinification (yield 30%).

SUMMARY

1. It is shown that heating of quinoline with formamide or formic acid (preferably in presence of sodium formate) leads to reduction of the pyridine ring and simultaneous formylation.

2. A method is developed for synthesis of N-formyl-1,2,3,4-tetrahydroquinoline in 85% yield; it readily hydrolyzes to 1, 2, 3, 4-tetrahydroquinoline.

LITERATURE CITED

[1] R. Lukes, Collect. Czech. Chem., 10, 66 (1938); 12, 71 (1947).

[2] F. R. Mayo, J. Org. Chem., 1, 496 (1936).

[3] A. N. Kost and I. I. Grandberg, J. Gen. Chem., 25, 1432 (1955). (T.p. 1377)*

[4] I. I. Eru, E. M. Sakhnovskaya and V. A. Pychko, J. Gen. Chem., 8, 1567 (1938).

[5] Z. Hofmann, W. Konigs, Ber., 16, 727 (1883).

[6] A. N. Vyshnegradsky, Ber., 12, 1481 (1880).

Received December 13, 1954

Moscow State University

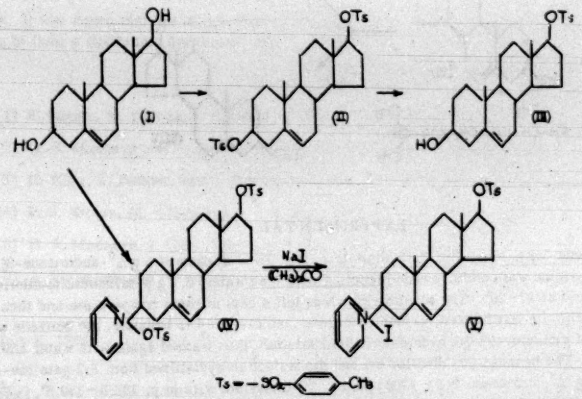
* T.p. = C. B. Translation pagination.

SOME PROPERTIES OF ESTERS OF p-TOLUENESULFONIC ACID AND 17β-HYDROXYSTEROIDS

IV. QUATERNARY PYRIDINIUM SALTS OF Δ^5-ANDROSTENE-3(β), 17(β)-DIOL DITOSYLATE

O. S. Madaeva and N. P. Babanova

In the course of study of the so-called retro compounds, we developed a synthesis of the 17-tosylate of Δ^5-androstene-3(β), 17(β)-diol 17-tosylate (III).



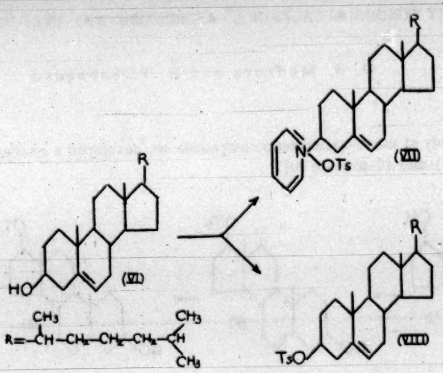
Preparation of (III) is based on the differing susceptibilities of the tosyloxy groups of Δ^5-androstene-3(β), 17(β)-diol ditosylate (II) to saponification when heated in aqueous acetone; under these conditions the 3(β)-tosyl ester is saponified completely while the 17(β)-tosyl ester remains unchanged.

It was observed that formation of (II) necessitates the carrying out of the reaction of (I) with p-toluenesulfochloride in pyridine solution at room temperature; quaternary pyridinium salts are formed at higher temperatures; at 70–75°, even for 30 minutes, a white, benzene-insoluble crystalline precipitate is formed which corresponds in composition to the quaternary mono pyridinium salt of Δ^5-androstene-3(β), 17(β)-diol ditosylate (IV). From it was got the quaternary pyridinium iodide (V) by reaction with sodium iodide in acetone solution at room temperature [1].

We showed previously [2] that the transformation of the 17-tosyl ester into the quaternary pyridinium salt requires very drastic conditions (heating in pyridine at about 200° for upward of 20 hours). Consequently, under the conditions of formation of the ditosylate the formation of the C_{17}-quaternary pyridinium salt is excluded: it can only be formed at C_3. However, heating under such conditions of cholesterol (VI) in pyridine solution with p-toluenesulfochloride leads only to the tosylate of cholesterol (VIII) which remains unchanged on further heating in pyridine at 75° for 30 minutes. According to the literature the quaternary pyridinium salt of cholesteryl tosylate (VII) is obtained by heating on a steam bath for 5½ hours [3].

Apparently the superior mobility of the tosyloxy group at C_3 in the ditosylate (II) in comparison with cholesteryl tosylate (VIII) is accounted for by the influence of the tosyloxy group at C_{17}.

Tipson [4], in a study of the properties of tosyl esters of various organic compounds, observed that tosylates incapable of entering into double decomposition reactions with sodium iodide in acetone form quaternary pyridinium salts with difficulty. His observation is also confirmed in the series of the steroid compounds: whereas tosyl esters in the C_3 position capable of forming a quaternary pyridinium salt readily give 3-iodo derivatives with sodium iodide in acetone solution, the 17-tosylates, as we have shown [5], entirely fail to react with sodium iodide under these conditions.



EXPERIMENTAL

Δ^5-Androstene-3(β), 17(β)-diol 3,17-ditosylate (II). To a solution of 5 g Δ^5-androstene-3(β), 17(β)-diol in 15 ml dry pyridine was carefully added (cooling with iced water) 6.7 g p-toluenesulfochloride, the temperature being held at 17–20°. The reaction mass was left 4 days at room temperature and then poured into water. The precipitate was filtered, washed with water and dissolved in benzene; the benzene solution was washed free from pyridine with 2% hydrochloric acid solution, then washed again with water and dried with sodium sulfate. The benzene was distilled off and the residue recrystallized from 1:2 gasoline-acetone mixture to give 7.3 g Δ^5-androstene-3(β), 17(β)-diol 3, 17-ditosylate with m.p. 138.5–139.5°, $[\alpha]_D^{20}$ –59° (1% solution in chloroform); the literature [6] reports m.p. 140–141°.

Δ^5-Androstene-3(β), 17(β)-diol 17-tosylate (III). 7.3 g Δ^5-androstene-3(β), 17(β)-diol 3, 17-ditosylate was dissolved with stirring in 730 ml pure acetone freed from traces of alcohol; 420 ml water and 0.3 g magnesium carbonate were added and the mixture boiled 4 hours. The acetone was taken off and the precipitate dissolved in ether; the ethereal solution was washed with water and dried with sodium sulfate. The ether was then distilled off. Recrystallization of the residue from alcohol gave 3.44 g (III) with m.p. 128.5–129.5°. A mixed test with Δ^5-androstene-3(β), 17(β)-diol 17-tosylate, obtained by saponification of Δ^5-androstene-3(β), 17(β)-diol 3-acetate, 17-tosylate [2], did not give a depression of the melting point. From the filtrate was isolated a further 0.82 g product with m.p. 125–127°.

3-Monopyridinium salt of Δ^5-androstene-3(β), 17(β)-diol ditosylate (IV). 0.5 g Δ^5-androstene-3(β), 17(β)-diol was dissolved in 2 ml anhydrous pyridine and 0.98 g p-toluenesulfochloride was added; the mixture was heated at 70° for 30 minutes and left until the following day at room temperature. The mixture was then poured into water; a white, benzene-insoluble precipitate came down; this was filtered, washed with 2% hydrochloric acid solution and then with water, and dried at 60°; m.p. 132–134°. The substance is insoluble in a mixture of gasoline and acetone (1:2). After recrystallization from acetone it has m.p. 139–140° (in sealed capillary), $[\alpha]_D^{20}$ –29.83° (1% solution in chloroform). A mixed test with (IV) does not give a depression of m.p.

Found %: C 65.35; H 7.23; N 2.15; S 9.38, 9.57. $C_{38}H_{47}O_6NS_2$. Calc. %: C 65.57; H 7.10; N 2.00; S 9.20.

Monopyridinium salt of 3-iodo-17-tosylate of Δ^5-androstene-17(β)-ol (V). To 0.15 g 3-monopyridinium salt of Δ^5-androsten-3(β), 17(β)-diol ditosylate in 20 ml acetone was added 0.15 g sodium iodide at room temperature; a precipitate of the sodium salt of p-toluenesulfonic acid at once started to come down. The acetone was driven off from the filtrate. After two hours this precipitate was filtered off. The acetone was driven off from the filtrate in vacuum and the dry residue transferred to a filter and washed with water, benzene and a few drops of cooled acetone. The faint-yellow product had m.p. 177–179°. After dissolving in acetone and reprecipitating with ether the m.p. was 183–183.5°.

Found %: C 58.35, 58.62; H 6.49, 6.46; N 2.10 (Kjeldahl), 2.20 (Dumas); S 5.11; I 19.46. $C_{31}H_{40}O_3$ NSI. Calc. %: C 58.74; H 6.37; N 2.21; S 5.05; I 20.04.

SUMMARY

1. A simple method is given for the preparation of Δ^5-androstene-3(β), 17(β)-diol 17-tosylate.

2. The quaternary pyridinium salts of Δ^5-androstene-3(β), 17(β)-diol 3, 17-ditosylate and of Δ^5-androsten-17(β)-ol 3-iodo-17-tosylate were prepared.

3. It was shown that the introduction of the tosyl residue at C_{17} enhances the ability of the tosyl ester at C_3 to form a quaternary pyridinium salt.

LITERATURE CITED

[1] E. Rogers, W. Leanza, J. Conbere, K. Pfister, J. Am. Chem. Soc., 74, 2947 (1952).

[2] O. S. Madaeva and F. A. Luri, Proc. Acad. Sci. USSR, 84, 713 (1952).

[3] C. King, R. Dodson, and L. Subluskey, J. Am. Chem. Soc., 70, 1176 (1948).

[4] R. S. Tipson, M. Clapp and L. Cretcher, J. Org. Chem., 12, 133 (1947).

[5] O. S. Madaeva, J. Gen. Chem., 25, 1427 (1955). (T.p. 1373)*

[6] A. Butenandt and W. Grosse, Ber., 70, 1447 (1937).

Received July 8, 1954

S. Ordzhonikidze Scientific Research Institute of Pharmaceutical Chemistry

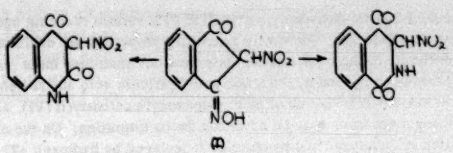
* T.p. = C. B. Translation pagination.

THE BECKMANN REARRANGEMENT OF 2-NITROINDANEDIONE-1,3 OXIME

G. Ya. Vanag and V. N. Vitol

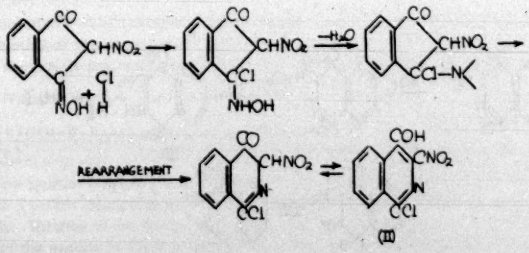
The Beckmann rearrangement of oximes of cyclic ketones usually proceeds in such a manner that the nitrogen enters the ring, the latter becoming expanded and forming a lactam. Thus, for instance, the Beckmann rearrangement of cyclohexanoneoxime gives the lactam of ε-aminocaproic acid which polymerizes to "caprone" [1–3]. Analogous rearrangements take place with ketones of condensed systems, and then two isomeric lactams may be formed, for example from the oxime of β-tetralone [4]. In the case of dioximes of cyclic diketones both oxime groups can rearrange; thus the dioxime of cyclohexanedione-1,4 gives two isomeric lactams with an 8-membered ring [5].

In the Beckmann rearrangement of the monoxime of nitroindanedione (I) we should, by analogy, theoretically expect the formation of a derivative of quinoline as well as a derivative of isoquinoline [6].



(I)

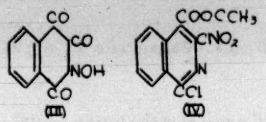
The Beckmann rearrangement of nitroindanedioneoxime proceeds readily under the action on the oxime of Beckmann mixture as well as of phosphorus oxychloride, phosphorus trichloride, acetyl chloride and benzoyl chloride [7]. In all cases one and the same substance is obtained, namely 1-chloro-3-nitro-4-hydroxyisoquinoline (II). Its formation can be explained by the usual scheme of rearrangement: addition of hydrogen chloride followed by loss of water and rearrangement:



(II)

In the Beckmann rearrangement of ketoximes the addition of hydrogen chloride is usually regarded as an intermediate phase of the reaction; then follows hydrolysis of the chloro derivative and replacement of its chlorine by the hydroxyl group. In our case the corresponding chloro derivative (II) was a stable end product of the reaction. That the compound was a derivative of isoquinoline and not of quinoline was shown by its cleavage and oxidation. The final product was phthalic acid or phthalimide. The ease of transition of isoquinoline derivatives to phthalimide has been repeatedly noted in the literature. Treatment of 1-chloro-3-nitro-4-hydroxyisoquinoline with caustic alkali gives in solution both chloride and nitrite. This indicates that the nitro group had remained intact during the Beckmann rearrangement of the oxime of nitroindanedione.

As was shown earlier [8], isomerization of nitroindanedione in presence of acetic anhydride gives N-hydroxyphthaloneimide (III). The location of the hydroxyl group of 1-chloro-3-nitro-4-hydroxyisoquinoline was verified by the preparation of the corresponding acetyl derivative (IV):

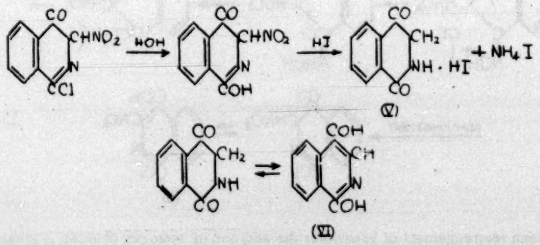


(III) (IV)

We have thus verified all the functional groups of the product of Beckmann rearrangement of nitroindanedioneoxime. One fact remained to be established, however: that this product is indeed a derivative of isoquinoline. That special care is here necessary is clear from the already known properties of nitroindanedione – its facile transformation into derivatives of both phthaloneimide and phthalide [9].

Isoquinoline is often obtained when many derivatives of isoquinoline are distilled with zinc dust. On applying this method to our product of rearrangement as well as to some of its derivatives, we always obtained a distillate with the odor of isoquinoline; we were unable, however, to isolate it. This may be due to the facility of decomposition of the product of rearrangement. In the distillate were detected phthalimide and certain violet substances (phthalocyanines?) which interfered with the separation of the isoquinoline in the form of the picrate.

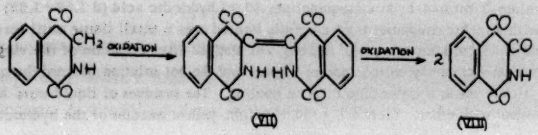
Reduction of 1-chloro-3-nitro-4-hydroxyisoquinoline with various reducing agents under various conditions did not give crystalline substances. Some very interesting properties are exhibited by the compounds obtained, but due to the difficulty of their purification they were not examined more closely. Finally we succeeded in obtaining a crystalline compound by reduction with hydriodic acid and red phosphorus. The main product of the reaction was 1,4-dihydroxyisoquinoline or 4-hydroxyisocarbostyril (VI), already described in the literature [10]. The following mechanism may be advanced for its formation. On the one hand 1-chloro-3--nitro-4-hydroxyisoquinoline is hydrolyzed and its chlorine is replaced by hydroxyl. The facility of hydration of the azomethine bond in isoquinoline derivatives has been reported in the literature [11]. That the accumulation of oxygen atoms and negative groups greatly facilitates hydrolysis of cyclic systems has been demonstrated very recently by Soviet chemists in a series of investigations (see, for example [12 and 13]). On the other hand the nitro group is split off in the process of reduction with formation of ammonium iodide which can actually be isolated from the filtrate in large amount. The entire reduction scheme is represented as follows:



(VI)

One of the most interesting properties of 1,4-dihydroxyisoquinoline is the ease with which it oxidizes to carbindigo [10]. Fuming nitric acid oxidizes carbindigo (VII) to phthaloneimide (VIII). Our reduction product likewise exhibited these properties:

Further confirmation of the identity of the prepared 1,4-dihydroxyisoquinoline was obtained by preparation of its products of condensation with phthalic anhydride and benzaldehyde. The properties of these derivatives were in full accord with the literature data.



EXPERIMENTAL

1-Chloro-3-nitro-4-hydroxyisoquinoline

1. 10 g nitroindanedioneoxime and 200 ml Beckmann mixture (400 g glacial acetic acid and 100 g acetic anhydride saturated with hydrogen chloride) were refluxed on a water bath. The oxime dissolved to give a yellow solution. On cooling, a yellow crystalline substance came down. Water was added for complete precipitation, and the product was suction-filtered and washed with water. Yield of 1-chloro-3-nitro-4-hydroxyisoquinoline 7.3 g (67%). The compound crystallizes well from many organic solvents, for example glacial acetic acid, alcohol, chloroform, and dioxane. White needles with m.p. 212–213°.

2. 10 g nitroindanedioneoxime, 100 ml glacial acetic acid and 10 ml phosphorus oxychloride (or phosphorus trichloride) were refluxed on a water bath. The oxime dissolved to form a yellow solution. After cooling, the mixture was diluted with water, suction-filtered, and worked up as previously. Yield 8.4 g (77%).

3. Into a flask with an air condenser (ground-glass connection) were introduced 10 g nitroindanedioneoxime, 100 ml glacial acetic acid and 10 ml phosphorus oxychloride. Reaction commenced after 5–10 minutes; heat was generated, hydrochloric acid was evolved, and the yellow crystals of nitroindanedioneoxime were gradually transformed into white needles. The reaction goes without external heating and is completed in 2 hours. The mixture was gradually diluted with water and worked up as previously. Yield 9.3 g (85.3%).

Found %: N 12.41; Cl 15.95. M 222.8 (Rast), 226.1 (in ethylene bromide). $C_9H_5O_3N_2Cl$. Calc. %: N 12.48; Cl 15.80. M 224.5.

2 g 1-chloro-3-nitro-4-hydroxyisoquinoline was covered with 15 ml concentrated sulfuric acid and heated on a water bath. The liquid darkened and gave off hydrochloric acid. When the latter ceased to come off the liquid was run into water. The next day the yellowish needles of phthalimide were separated. M.p. 234°. It sublimed. Ammonia is evolved on heating with caustic alkalies. No melting point depression in admixture with pure phthalimide.

To a suspension of 1-chloro-3-nitro-4-hydroxyisoquinoline in water, heated on a water bath, was added an aqueous solution of potassium permanganate until decolorization no longer occurred. The liquid was filtered. From the filtrate separated pale-yellow, long needles of phthalimide. Identification as before.

Found %: N 9.48. $C_8H_5O_2N$. Calc. %: N 9.52.

Acetate of 1-chloro-3-nitro-4-hydroxyisoquinoline (1-chloro-3-nitro-4-acetoxyisoquinoline)

1 g 1-chloro-3-nitro-4-hydroxyisoquinoline and 5 ml acetic anydride were boiled until the solid dissolved. The cooled yellow solution deposited light-yellow needles of the acetate of 1-chloro-3-nitro-4-hydroxyisoquinoline. Dilution of the filtrate with water (after decomposition of the acetic anhydride) brought down a little more of the acetate in the form of white needles. Total yield 1 g (77%). Crystallization from alcohol, acetic acid or other solvents gave white needles with m.p. 136°.

Found %: N 10.57; Cl 13.25. M 255.4 (Rast), 282.4 (in acetone). $C_{11}H_7O_4N_2Cl$. Calc. %: N 10.52; Cl 13.30. M 266.5.

The odor of ethyl acetate was detected when the acetate of 1-chloro-3-nitro-4-hydroxyisoquinoline was heated with concentrated sulfuric acid.

1,4-Dihydroxyisoquinoline

10 g 1-chloro-3-nitro-4-hydroxuisoquinoline, 40 ml hydriodic acid (d 1.52–1.62) and 10 g red phosphorus in a flask with a reflux condenser were carefully heated over a small flame until reaction commenced. Gases came off and much frothing occurred. Heating was stopped after cessation of the violet reaction (5–7 minutes); then the mass was gently boiled another 2 hours and the hot solution filtered through a glass filter. The light-yellow filtrate set to a crystalline mass on cooling. The residues of liquid were filtered at the pump and the crystals washed with ether. Yield 7.8 g (60.6%) light-yellow needles of the hydroiodide of dihydroxyisoquinoline (V).

Found %: N 4.59; I 43.53. $C_9H_9O_2NI$. Calc. %: N 4.85; I 43.91.

The salt hardly dissolves when heated with water but hydrolyzes with formation of a yellow, amorphous substance – 1,4-dihydroxyisoquinoline (VI). It can be crystallized from alcohol, glacial acetic acid, acetone and other solvents. The solutions at first are yellow but gradually redden on standing due to oxidation of the 1,4-dihydroxyisoquinoline to carbindigo. This change is particularly conspicuous in acetic acid solution in which oxidation goes most rapidly with deposition of the dark-red carbindigo (VII); in order, therefore, to obtain light 1,4-dihydroxyisoquinoline, the crystals must be filtered quickly after cooling of the solution. 1,4-Dihydroxyisoquinoline becomes red at about 200° but does not melt even at 250°.

Found %: N 8.49. $C_9H_7O_2N$. Calc. %: N 8.70.

To a saturated solution of 1,4-dihydroxyisoquinoline in alcohol was added a saturated solution of picric acid in alcohol. Yellow crystals of the picrate of 1,4-dihydroxyisoquinoline came down; m.p. 218°.

Found %: N 14.16. $C_{15}H_{10}O_9N_4$. Calc. %: N 14.36.

Oxidation of 1,4-dihydroxyisoquinoline to carbindigo

1. 1 g of the prepared 1,4-dihydroxyisoqunioline hydroiodide in a porcelain dish was covered with 10 ml water; 2% potassium hydroxide was added with stirring until the liquid and precipitate were red; the mass was then heated on a water bath.

Part of the solution was evaporated to leave a liquid with a red-brown solid. The latter was collected, washed with hot water and boiled with alcohol. The residual carbindigo was crystallized from nitrobenzene. Dark-red crystals with m.p. above 400°.

Found %: N 8.76. $C_{18}H_{10}O_4N_2$. Calc. %: N 8.81.

2. To a suspension of the prepared 1,4-dihydroxyisoquinoline in water was added hydrochloric acid and hydrogen peroxide; the mixture was boiled. The yellow 1,4-dihydroxyisoquinoline was transformed into red carbindigo. The latter formed an orange-yellow solution in caustic alkali; in nitrobenzene the color is dark-red; from the latter solution were isolated dark-red crystals of carbindigo with m.p. 400°.

Found%: N 9.02. $C_{18}H_{10}O_4N_2$. Calc. %: N 8.81.

Oxidation of carbindigo to phthaloneimide

0.15 g carbindigo, prepared in the preceding experiment, and 2 ml fuming nitric acid were heated until a yellow solution was formed. It was cooled and pieces of ice introduced. Yellow needles of phthalone-imide (VIII) came down. Yield 0.1 g. M.p. 224–225° after crystallization from water.

Found %: N 8.02. $C_9H_5O_3N$. Calc. %: N 8.00.

SUMMARY

The Beckmann rearrangement of 2-nitroindanedione-1,3-oxime with the help of Beckmann mixture, phosphorus oxychloride, phosphorus trichloride and other reagents gives 1-chloro-3-nitro-4-hydroxyisoquinoline.

Reduction of 1-chloro-3-nitro-4-hydroxyisoquinoline with hydriodic acid and red phosphorus gave 1,4-dihydroxyisoquinoline.

The possibility was thereby proved of transition from relatively easily available derivatives of indanedione to new derivatives of isoquinoline. A derivative of isoquinoline with a nitro group in the pyridine

ring was obtained; compounds of this type have not hitherto been described in the literature.

LITERATURE CITED

[1] I. Knunyants, Z. Rogovin, Yu. Rymasheveskaya and E. Khait, J. Gen. Chem., 17, 987 (1947).

[2] Z. Rogovin, E. Khait, I. Knunyants, Yu. Rymasheveskaya, J. Gen. Chem., 17, 1316 (1947).

[3] Z. Rogovin, A. Strepikheev and A. Prokofyeva, J. Gen. Chem., 17, 1321 (1947).

[4] I. L. Knunyants and B. P. Fabrichnyi, Proc. Acad. Sci. USSR, 68, 523 (1949).

[5] I. L. Knunyants and B. P. Fabrichnyi, Proc. Acad. Sci. USSR, 68, 701 (1949).

[6] G. Vanag and E. Vitol, Bull. Acad. Sci. Latvian SSR, No. 7 (60), 107 (1952).

[7] V. Vitol, New Method of Synthesis of Isoquinoline Derivatives, Dissert., Riga (1952).

[8] G. and E. Vanag, Proc. Acad. Sci. USSR, 90, 59 (1953).

[9] G. Ya. Vanag and V. N. Vitol, Proc. Acad. Sci. USSR, 89, 857 (1953).

[10] S. Gabriel and J. Colman, Ber., 33, 996 (1900).

[11] H. Davies, T. H. Ramsay and E. R. Stove, J. Chem. Soc., 1949, 2633.

[12] M. M. Shemyakin, L. A. Shchukina, Yu. V. Shvetsov, D. P. Vitkovsky and A. S. Khokhlov, J. Gen. Chem., 21, 1667 (1951). (T.p. 1831)•

[13] D. P. Vitkovsky and M. M. Shemyakin, J. Gen. Chem., 21, 1033 (1951), (T.p. 1131)•

Received October 11, 1954

Institute of Chemistry Academy of Sciences of the Latvian SSR

• T.p. = C. B. Translation pagination.

SYNTHESES WITH THE HELP OF ACRYLONITRILE

XXI. SYNTHESIS AND PROPERTIES OF N-INDOLYL-β-PROPIONIC ACIDS

A. P. Terentyev, A. N. Kost and V. A. Smit

Substituted indoles in presence of alkaline agents react with acrylonitrile to give N-(β-cyanoethyl)-derivatives [1]. The catalyst chiefly used was "Triton B" (40% aqueous solution of trimethylbenzylammonium hydroxide). We showed previously, with reference to the cyanoethylation of α-phenylindole and carabazole [2], that "Triton B" can be advantageously replaced by Rodionov catalyst (alcoholic solution of ethoxytrimethylphenylammonium). The only information about the cyanoethylation of indole itself has appeared in patents [3-5]. Thus, Roh and Wolf [3] point out that heating of indole with acrylonitrile (5 hours, 120-130°) in presence of sodium ethoxide and copper borate leads to N-indolyl-β-propionitrile in 89% yield. At the same time some 1,3-dinitrile is formed, the constants of which are not stated. Reppe and Ufer [5] claim that in an acid medium (acetic or boric acid) cyanoethylation likewise occurs in the 1-position, while with addition of copper borate it occurs in the 3-position.

Our experiments show that indole and acrylonitrile do not react without a catalyst even on intensive heating (20 hours, 200°). Joint heating of the components in presence of sodium ethoxide gives an insignificant yield of N-indolyl-β-propionitrile since a considerable amount of the acrylonitrile polymerizes. In presence of copper salts in an alkaline medium polymerization is suppressed but not completely. If, however, the reaction is conducted in an inert solvent (benzene) in presence of potassium hydroxide, heating is not required. The reaction goes in 1-2 hours at room temperature (with slight heat development), giving perfectly pure N-indolyl-β-propionitrile (traces of the 1,3-dinitrile were absent).

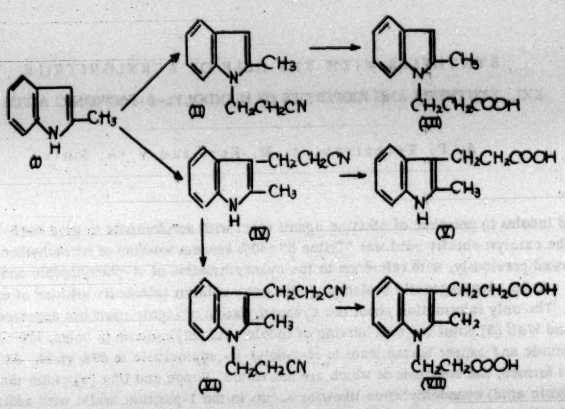
It is desirable to take a double excess of acrylonitrile since otherwise (even with 7 hours heating to 120-140°) a part of the indole does not enter into reaction. The amount of potassium hydroxide is also important. The optimum was found to be 5-6 g potassium hydroxide per mole indole (yield 95%); reduction in the amount of alkali to 1 g leads to a sharp drop in yield (30%), and increase to 40 g led to considerable polymerization of the acrylonitrile and to a corresponding fall in yield (80%). Heating of the mixture does not increase but slightly reduces the yield due to polymerization of the acrylonitrile (2 hours, 120-140°; yield 88-90%). Consequently the conditions specified in the patent appear too drastic. In presence of acidic additions (boric or acetic acid) even at 200°, the reaction does not go (between 85 and 90% of the indole was recovered unchanged).

In our selected reaction conditions (potassium hydroxide, in benzene solution without heating) cyanoethylation in the 1-position takes place smoothly also with a number of other indole compounds. Thus, β-indolyl-β-propionitrile (XII) and β-(α-methylindolyl)-β-propionitrile (IV) gave the dinitriles in yields of 97 and 83% respectively. α-Methylindole (I) requires slight heating (1 hour on water bath). Saponification of all the above-mentioned nitriles and dinitriles gave the corresponding acids.

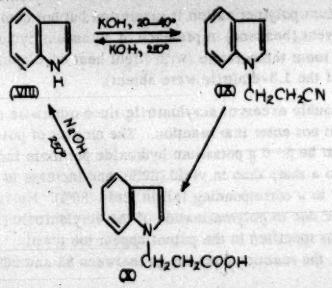
Saponification of N-(α-methylindolyl)-β-propionitrile (II) gave (α-methylindolyl)-β-propionic acid (III) with m.p. 111-112°. Roh and Wolf reported [3] m.p. 110° for this compound; Reppe [5], however, gave m.p. 135°. Reppe's constants agree better with β-(α-methylindolyl)-β-propionic acid (V) for which is reported m.p. 138° [6]. By hydrolysis of β-(α-methylindolyl)-β-propionic acid we obtained this acid with m.p. 138°.

It should be mentioned that Reppe's error was not fortuitous, since he also erroneously attributes to the product of addition of maleic anhydride to α-methylindole [5] the structure of N-(α-methylindolyl)-succinic acid, whereas Diels and Alder [7] had previously described this reaction and has shown that the substance formed is β-(α-methylindolyl)-succinic acid.

N-Indolyl-β-propionic acid (X) and its nitrile (IX) are perfectly stable compounds, distillable in vacuum without decomposition. However, after 8 hours boiling of N-indolyl-β-propionitrile (IX) with concentrated

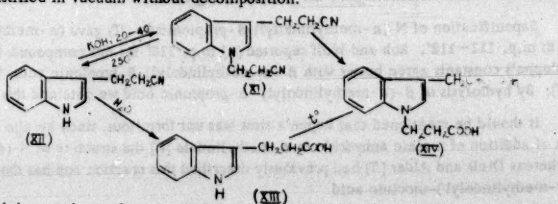


potassium hydroxide solution (with or without passage of a stream of ammonia), not only is the nitrile hydrolyzed but the indole (VIII) is partly cleaved (up to 10%), whereas the corresponding N-indolyl-β-propionic acid (X) is stable under these conditions. Quantitative cleavage of the β-carboxyethyl group was effected by treatment of an alkaline solution of N-indolyl-β-propionic acid with steam superheated to 250–270°.



Similar treatment with steam of N,β-indolydene-di-β-propionic acid (XIV) gives β-indolyl-β-propionic acid (XIII) which is fully stable under these conditions.

The dinitrile of N,β-indolydene-di-β-propionic acid (XI) is less stable than the corresponding mononitrile: on heating in vacuum to 250° it loses acrylonitrile with quantitative formation of β-indolyl-β-propionitrile (XII) which can be distilled in vacuum without decomposition.



It is thus confirmed that products of cyanoethylation in which the β-cyanoethyl group is linked to a hetero atom are susceptible to facile cleavage into the original components and to transcyanoethylation due to the lability of the bond between the hetero atom and carbon. But if a carbon-carbon bond was established

in the process of cyanoethylation, then such compounds split off the cyanoethyl group only with great difficulty [8].

We also carried out a series of experiments on the reaction of indole (in an alkaline medium) with ethylene cyanohydrin, β-alkoxypropionitriles and dimethylaminopropionitrile. The direction of reaction in these cases was difficult to predict because although acrylonitrile in an alkaline medium cyanoethylates indole only in the 1-position, alcohols in an alkaline medium give β-alkylindoles with indole [9], and condensations of Mannich bases with indole in the β-position have also been described [10]. It was found that heating of ethylene cyanohydrin with indole in an autoclave in presence of alkali (6–12 hours, 150–200°) gives after hydrolysis 40–90% yields of N-indolyl-β-propionic acid (X); the product, however, is much less pure than in the synthesis with the help of acrylonitrile (β-substituted indoles could not be isolated). Similarly the reaction with β-dimethylaminopropionitrile gave this acid in 47% yield, while reaction with β-dimethylaminoethoxy propionitrile gave it in a yield of 53%.

Ethyl acrylate is more sluggish than acrylonitrile in its reaction with indole. The reaction barely goes without heating, while with 2 hours heating (in an alkaline medium) up to 80°, ethyl N-indolyl-β-propionate was obtained in a yield of 30%.

EXPERIMENTAL

Use was made in all experiments of perfume-grade indole, distilled in vacuum, and of acrylonitrile dried with calcium chloride and stabilized with hydroquinone.

N-Indolyl-β-propionitrile (IX). In a three-necked flask, fitted with reflux condenser and stirrer, was placed a solution of 11.7 g indole and 10.6 g acrylonitrile in 50 ml anhydrous benzene; the stirrer was started and 0.6 g pulverized potassium hydroxide was added; the mixture almost at once acquired a blue color which later changed to red. After 20–30 minutes the temperature of the mixture rose spontaneously to 30–40°. After 1–2 hours, the stirrer was stopped and the benzene solution filtered from the small amount of solid; the benzene and excess acrylonitrile were driven off on a water bath and the residue distilled in vacuum. The greater part came over at 168–180° (3 mm) in the form of a colorless oil which at once solidified on cooling. Yield 16.2 g (95%) N-indolyl-β-propionitrile (IX) with m.p. 47°. Literature data: m.p. 47–48°, b.p. 170–183° at 1 mm [5], 154–156° at 1 mm [3].

Hydrolysis of N-indolyl-β-propionitrile. A mixture of 17 g N-indolyl-β-propionitrile and 150 ml 10% potassium hydroxide solution was boiled 3 hours (until the oily layer had completely dissolved). The solution was filtered, cooled externally with ice and acidified with hydrochloric acid (3:1) (test with congo) to separate N-indolyl-β-propionic acid in the form of a white resin which immediately crystallized. The crystals were filtered, washed quickly with cold water and dried in a desiccator over calcium chloride. Yield 18.0 g (95%) N-indolyl-β-propionic acid (X) with m.p. 85–86°.

The acid was purified by dissolving in 70 ml alcohol, filtering, and reprecipitating the acid by dropwise addition of 120 ml water with good cooling and stirring. Pure N-indolyl-β-propionic acid came down in the form of white crystals. Yield 15 g acid with m.p. 90–91°. Literature data: m.p. 91°, b.p. 180–190° (without mention of the pressure [5]).

β-Indolyl-β-propionic acid (XIII) with m.p. 133° was similarly obtained by boiling 17 g β-indolyl-β-propionitrile (XII) b.p. 190–210° at 3 mm, m.p. 67–68° (from benzene); literature data: m.p. 64° [5] for 2 hours with 80 ml 25% potassium hydroxide solution followed by addition of 10% hydrochloric acid. Yield 17 g (90%). From β-(α-methylindolyl)-β-propionitrile (IV) [5], b.p. 203–209° at 2 mm, m.p. 79.5° (from aqueous methanol), was obtained a 70% yield of β-(α-methylindolyl)-β-propionic acid (V) with m.p. 138°; literature data: m.p. 138° [6].

Cyanoethylation of indole with ethylene cyanohydrin. A solution of 11.7 g indole, 8 g ethylene cyanohydrin and 6 g solid potassium hydroxide in 100 ml 95% ethyl alcohol was heated in a 500 ml steel autoclave for 6 hours at an oil bath temperature of 190–200°. After cooling, the autoclave was opened; the solvent was driven off on a boiling water bath, then the unreacted indole (2.5 g) was distilled off with steam, after which the solution was boiled with active carbon, filtered, cooled, and acidified with hydrochloric acid (1:3) until acid to congo; N-indolyl-β-propionic acid (X) came down in the form of a resin which solidified in the cold to a light-brown mass. This was filtered, washed with cold water and dried over calcium chloride.

Yield 9 g with m.p. 82° (47 % reckoned on the weight of indole or 62% on the reacted indole).

After recrystallization from aqueous alcohol, N-indolyl-β-propionic acid has m.p. 86°. It distils (preferably in a nitrogen stream) at 180 – 190° and 2 mm in the form of a colorless oil which solidifies on cooling. It is readily soluble in alcohol, ether, benzene and dichloroethane; it crystallizes from gasoline or ligroine in the form of small, colorless needles with m.p. 89°. By reprecipitation with hydrochloric acid from alkali solution, the acid is obtained with m.p. 91°. A mixture with a specimen of N-indolyl-β-propionic acid obtained by hydrolysis of the nitrile does not give a depression of melting point.

A lower yield (41%) is obtained when using sodium hydroxide as the catalyst. The best results are got by heating 0.1 mole indole, 0.1 mole ethylene cyanohydrin and 0.25 mole potassium hydroxide (in 100 ml alcohol). The reaction in this case took 6 hours at 220° (bath temperature) and the yield was 90%; however, the acid has a m.p. of about 70° and was difficult to free from products of resinification.

Cyanoethylation of indole with β-ethoxypropionitrile. A solution of 5.9 g indole, 7.5 g β-ethoxypropionitrile and 4.1 g solid potassium hydroxide in 50 ml 95% ethyl alcohol was heated in a 90 ml steel autoclave for 6 hours at an oil bath temperature of 190–200°. Separation of the N-indolyl-β-propionic acid was effected as in the experiment with ethylene cyanohydrin. There was obtained 4.4 g N-indolyl-β-propionic acid (X) with m.p. 76–78°, or about 47%.

Attempts to conduct the reaction in a medium of boiling benzene with stirring for 2–3 hours in presence of solid potassium hydroxide gave a negative result. Performance of the reaction in a medium of boiling xylene led to a 12% yield of N-indolyl-β-propionic acid with b.p. 160–165° at 2 mm (much of the indole was recovered).

Cyanoethylation of indole with β-dimethylaminopropionitrile. a) When carrying out the reaction in an autoclave the ratio of reactants and the experimental conditions were the same as in the experiment with β-ethoxypropionitrile. 1.2 g indole was recovered (out of 5.9 g taken for the experiment). There was obtained 5 g N-indolyl-β-propionic acid with m.p. 77–78°, equivalent to a yield of 53% reckoned on the indole taken, and 65.7% on the reacted indole.

b) A mixture of 11.7 g indole, 19.6 g β-dimethylaminopropionitrile and 0.6 g dry, pulverized potassium hydroxide was heated with stirring in a medium of boiling xylene (50 ml) for 4 hours. The solution was filtered and heated on a water bath in the vacuum of a water jet pump to remove solvent and β-dimethylaminopropionitrile, after which the residue was vacuum-distilled to give 6 g indole and 3 g nitrile with b.p. 160–165° at 2 mm; hydrolysis of the latter gave N-indolyl-β-propionic acid (2.7 g) with m.p. 85–86°. The yield of acid was 15% reckoned on the indole taken and 30% on the reacted indole.

N-(α-methylindolyl)-β-propionic acid (III). A mixture of 3.9 g α-methylindole, 3.4 g acrylonitrile, 0.2 g dry, pulverized potassium hydroxide and 15 ml benzene was stirred one hour in the cold and one hour while heating on a water bath to the boil. The solution was filtered, the benzene and unreacted acrylonitrile were driven off on a water bath, and the residue distilled in vacuum. 0.6 g α-methylindole came over. The greater part of the reaction product came over at 170–180° (2 mm) in the form of a colorless, crystallizing oil. Yield 4.2 g (77%) N-(α-methylindolyl)-β-propionitrile (II) with m.p. 75–77°. After recrystallization from aqueous methanol the m.p. was 83°. A second recrystallization from aqueous methanol brought the m.p. to 84°, and this did not change on subsequent recrystallizations. Literature data: m.p. 82°, b.p. 180–194° at 2 mm [3].

A mixture of 1.8 g of the prepared nitrile with 10 ml 15% potassium hydroxide solution was boiled 3 hours. The solution was filtered; acidification in the cold with hydrochloric acid (1:3) gave N-(α-methylindolyl)-β-propionic acid (III) in the form of a resin which solidified in the cold. Yield 1.8 g (90%) acid with m.p. 108°, rising to 111–112° after crystallization from water. Literature data: m.p. 110° [3], 135° (?) [5].

Found %: N 6.79, 6.89, 7.01. $C_{12}H_{13}O_2N$. Calc. %: N 6.94.

N-Indolydene-di-β-propionic acid (XIV). A mixture of 34 g β-indolyl-β-propionitrile (XII) [5], 21.2 g acrylonitrile, 1.2 g dry, pulverized potassium hydroxide and 100 ml benzene was stirred 1–2 hours in the cold. 30–40 minutes after addition of the potassium hydroxide, the temperature of the solution had risen spontaneously to 30–40°. At the conclusion of the reaction, the yellow precipitate was filtered off, washed with a little benzene, and dried. Weight of precipitate 34 g, m.p. 95–96°. Evaporation of the mother liquor gave a further 9.1 g substance with m.p. 88–89°. Total yield of N,β-indolydene-di-β-propionile (XI) 43.1 g (97%).

After recrystallization from alcohol, 35.3 g dinitrile was obtained in the form of a light-yellow crystalline substance with m.p. 96–97°. Readily soluble in dichloroethane, chloroform and dioxane; soluble in benzene and ether; poorly soluble in carbon tetrachloride and ligroine. Two recrystallizations from alcohol gave white crystals with m.p. 97°.

Found %: C 75.10, 75.39; H 5.95. $C_{14}H_{13}N_3$. Calc. %: C 75.33; H 5.83.

A mixture of 6.7 g N,β-indolydene-di-β-propionitrile and 60 ml 10% potassium hydroxide solution was boiled 4 hours. After cooling, filtering and acidifying with hydrochloric acid (1:3), 7.4 g N,β-indolydene--di-β-propionic acid was obtained (94%) with m.p. 142°. After recrystallization from water the m.p. rose to 146° and remained constant on further crystallization from alcohol or acetone.

Found%: C 64.27, 64.35; H 5.70, 5.58. M (by titration) 264, 265. $C_{14}H_{15}O_4N$. Calc. %: C 64.36; H 5.74. M 261.2.

N,β-(α-Methylindolydene)-di-β-propionic acid (VII). A solution of 5.5 g β-(α-methylindolyl)-β--propionitrile (IV) and 3.2 g acrylonitrile in 15 ml benzene in presence of 0.2 g dry, solid potassium hydroxide was stirred without heating for 1–2 hours. Treatment of the reaction mixture and the procedure for isolation of the dinitrile were the same as in the preceding experiment. In all, 5.0 g (63%) dinitrile (VI) with m.p. 138° was obtained. Crystallizes from alcohol in the form of colorless needles with m.p. 143–144°. After 3 recrystallizations form alcohol, m.p. 144–145°. Literature data: m.p. 138° [7].

A mixture of 1.2 g N,β-(α-methylindolydene)-di-β-propionitrile (VI) and 10 ml of 15% potassium hydroxide solution was refluxed 4 hours. The usual treatment gave 1.30 g (quantitative yield) N,β-(α-methylindolydene)-di-β-propionic acid with m.p. 125–128°, rising to 128° after recrystallization from water. Literature: m.p. 128° [3].

Reaction of indole with ethyl acrylate in an alkaline medium. A solution of 5.8 g indole and 10.0 g ethyl acrylate in 25 ml benzene in presence of 0.3 g dry, pulverized potassium hydroxide was stirred 1 hour in the cold and then another 2 hours with heating on the water bath to the boiling point of benzene. The solution was filtered, the benzene was distilled off on a water bath, the excess of ethyl acrylate was distilled off in the vacuum of a water jet pump, and the residue distilled in vacuum to give 3.0 g unchanged indole and 3.1 g (30%) ethyl N-indolyl-β-propionate with b.p. 135–150° (2 mm). Alkaline hydrolysis of 1.1 g ester gave 0.9 g N-indolyl-β-propionic acid with m.p. 83–86° (no melting point depression with the pure acid).

Cleavage of the N,β-cyanoethyl and N,β-carboxyethyl groups

a) Steam superheated to 250–270° was passed into a solution of 5.7 g N-indolyl-β-propionic acid (X) in 10 ml 30% potassium hydroxide solution. The whole of the indole came over in the course of 20–40 minutes. There was obtained 2.5 g indole with m.p. 52°. Extraction of the aqueous distillate yielded a further 0.6 g indole. The total yield was substantially quantitative.

b) Steam superheated 280° was passed for 30–40 minutes into a solution of 3.9 g N,β-indolydene--di-β-propionic acid (XIV) in 10 ml 50% potassium hydroxide solution. The residue in the distillation flask was then dissolved in water, and the solution was filtered and acidified with hydrochloric acid (1:3); β-indolyl--β-propionic acid (XIII) came down in the form of white plates. After drying over calcium chloride the weight was 2.3 g (82%), m.p. 131°.

c) 5 g N,β-indolydene-di-β-propionitrile (XI) was heated with a small quantity of hydroquinone in a vacuum in a nitrogen stream at 250° (on a bath of Wood's metal). A white vapor came off and at 210° a transparent, crystallizable liquid started to distil over. The temperature then dropped and the main bulk came over at 190° (2 mm). There was obtained 3.4 g (92%) crystalline β-indolyl-β-propionitrile (XII) with m.p. 64°.

d) 5.7 g N-indolyl-β-propionic acid (X) was boiled in a 50% potassium hydroxide solution 8 hours with passage of ammonia. After boiling had ended, not even the slightest trace of indole came over on steam distillation. Acidification of the solution in the distillation flask led to the isolation of 4.6 g original acid.

e) 5.1 g N-indolyl-β-propionitrile (IX) was boiled in 25 ml of 50% aqueous potassium hydroxide solution for 8 hours with passage of ammonia. Steam distillation of the solution brought 0.5 g indole over. Acidification of the solution in the distillation flask gave 4 g N-indolyl-β-propionic acid (X).

SUMMARY

1. Methods are given for synthesis of N-indolyl-β-propionic acid and its nitrile (as well as of a series of analogs) in high yields, starting from indole compounds and acrylonitrile.

2. It was found that the β-cyanoethyl (and correspondingly the β-carboxyethyl) group can be split off if it is in the 1-position in indole, while it is stable if in the 3-position.

3. It was found that ethylene cyanohydrin, β-ethoxypropionitrile and β-dimethylaminopropionitrile in an alkaline medium react with indole similarly to acrylonitrile.

LITERATURE CITED

[1] A. P. Terentyev and A. N. Kost, The Cyanoethylation Reaction. Symposium on Reactions and Methods of Investigation of Organic Compounds, 2. State Chemical Publishing House, 47 (1952).

[2] A. P. Terentyev and A. N. Kost, Vestnik Moscow State Univ., 12, 71 (1950).

[3] N. Roh and W. Wolf, German Pat. 641597 (1935); British Pat. 457621 (1936); French Pat. 47563 (1937); Chem. Abs, 32, 4602 (1938).

[4] French Pat. 48570 (1937); Chem. Zentr., 1938, II, 3987.

[5] W. Reppe and H. Ufer, German Pat. 698273 (1940).

[6] I. Harley-Mason, J. Chem. Soc., 1952, 2433.

[7] O. Diels and K. Alder, Ann., 490, 277 (1931).

[8] A. P. Terentyev, A. N. Kost and S. M. Gurvich, J. Gen. Chem., 22, 1977 (1952); (T.p. 2027)• A. N. Kost and V. G. Yamunsky, J. Gen. Chem., 23, 230 (1953). (T.p. 239)•

[9] R. Cornforth and R. Robinson, J. Chem. Soc., 1942, 680.

[10] A. Butenandt, H. Hellman and E. Renz, Z. Phys. Chem., 284, 175 (1949).

Received October 20, 1954

Moscow State University

• T.p. = C. B. Translation pagination.

CONCERNING THE REACTION OF KETENE WITH NITROGEN-CONTAINING BASES

I. ACETYLATION OF UREA DERIVATIVES WITH KETENE

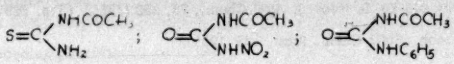
Yu. V. Svetkin and Yu. N. Forostyan

Direct acetylation of alcohols and amines by ketene has a number of advantages over other methods, mainly because the reaction goes under mild conditions.

The problem of the acetylation of alcohols by ketene has been admirably discussed in the review of A. Ya. Yakubovich [1] and in papers by A. A. Ponomarev and Yu. B. Isaev [2]. Concerning the reactions of ketene with the primary amino group, there is also an extensive literature [3]. Concerning secondary amines, Rice [4] reports that under appropriate conditions any compound containing the >NH group can be acetylated by ketene.

In our laboratory, experiments were carried out on the acetylation of urea derivatives by ketene.

All the experiments described below were performed at normal pressure and 18–20°. Solvents were benzene, toluene, carbon tetrachloride and dioxane; these substantially do not react with ketene. Urea derivatives have very poor solubility in these solvents, and the reactions were actually effected with the substances in suspension. Thiourea, nitrourea and monophenylurea were acetylated. On the basis of general theoretical considerations and the work of Ponomarev and Isaev, we should expect the formation of the following products:



However, direct reaction of ketene with the crystalline ureas in anhydrous solvents did not lead to acetates. Only on adding traces of water or acetic acid to the mixtures mentioned above does the reaction proceed energetically. Monoacetates of thiourea and nitrourea are formed in yields of 90–96%, the actual yield varying with the solvent. In spite of numerous attempts, the acetate of monophenylurea could not be obtained.

The high yields of monoacetylthiourea and monoacetylnitrourea obtained by addition of water or acetic acid may be attributed to a chain reaction.

The process evidently goes through the step of formation from ketene of acetic acid; the latter and ketene form acetic anhydride which acetylates the nitrourea with evolution of acetic acid; the latter reacts further with ketene.

EXPERIMENTAL

Acetylation of thiourea. Ketene was prepared by the method of Ponomarev and Isaev [5] with a constant rate of acetone feed of 50 ml per hour at 740°. In a three-necked flask with a mechanical stirrer 5 g thiourea (m.p. 182°) was put, triturated in 30 ml toluene with addition of 0.1 ml water• or 0.1 ml acetic acid. Ketene was then passed through the flask for 3 hours.

The temperature of the reaction mixture began to rise soon after the ketene was introduced (maximum temperature 42°). A drop of temperature marked the conclusion of the reaction. There was isolated 12 g crystals with m.p. 164–165° (from 1:1 acetic acid), in agreement with the literature [6].

Acetylation of nitrourea. 5.5 g nitrourea (m.p. 158.5°) was acetylated under similar conditions.

• Acetylation did not go in dry toluene, benzene, dioxane or carbon tetrachloride.

Ketene was passed through for 2 hours. The product (7.5 g) was recrystallized from acetone and had m.p. 115–116° (with decomp.).

Found %: C 24.45, 24.32; H 3.17, 3.24; N 28.21, 28.18. $C_3H_5O_4N_3$. Calc. %: C 24.49; H 3.42; N 28.57.

Acetylation of monophenylurea. 5.6 g monophenylurea (m.p. 147°) was acetylated. The process was carried out not only under the conditions described above but also in aqueous solution, in a mixture of acetone and water, with complete solution of the phenylurea, as well as in presence of sodium acetate at room temperature and with heating to 80°. Examination of the reaction products revealed that acetylation had not taken place. Acetylation of monophenylurea likewise does not go in the fused state.

SUMMARY

1. Monoacetylthiourea is obtained by acetylation of thiourea in toluene with addition of 0.1 ml water or acetic acid.

2. Reaction of nitrourea with ketene under these conditions gives monoacetylnitrourea.

3. Monophenylurea does not react with ketene under similar conditions.

LITERATURE CITED

[1] A. Ya. Yakubovich, Prog. Chem., 14, 301 (1945).

[2] A. A. Ponomarev and Yu. B. Isaev, J. Gen. Chem., 20, 1079 (1950); (T.p. 1121)• 21, 1045 (1951); (T.p. 1143)• 22, 652 (1952);(T.p. 715)•

[3] Ch. Hurd and C. Kocour, J. Am. Chem. Soc., 45, 2165 (1923).

[4] F. Rice, J. Greenberg, Ch. Waters and R. Uollrath, J. Am. Chem. Soc., 56, 760 (1936).

[5] A. A. Ponomarev and Yu. B. Isaev, J. Appl. Chem., 23, 222 (1950). (T.p. 229)•

[6] Chemists Handbook. State Chem. Press, 322 (1951).

Received January 11, 1955

Kishinev State University

• T.p. = C. B. Translation pagination.

SYNTHESIS OF BRANCHED TRIACETYLENIC HYDROCARBONS

PREPARATION OF 2,2,5,5,8,8,11,11-OCTAMETHYL-DODECATRIYNE-3,6,9,

A. I. Zakharova, G. D. Ilyina and G. M. Murashov

The literature on the synthesis of triacetylenes is very scanty. Up to the present only 9 representatives of triacetylenic hydrocarbons have been described, and all of them have triple bonds in the conjugated position. Thus, among the by-products of electrolytic synthesis of acetylene was detected an unsubstituted triacetylene (hexatriyne-1,3,5) [1]. This hydrocarbon was also obtained by special synthesis through several steps, starting from acetylene and formaldehyde [2]. Three representatives of monosubstituted triacetylenes are known: methyltriacetylene (heptatriyne-1,3,5), obtained by the reaction of the corresponding diacetylenic dichloride with sodium amide in liquid ammonia followed by alkylation with methyl iodide [2]; tert-butyltriacetylene (2,2-dimethyloctatriyne -3,5,7), formed as intermediate product in the synthesis of di-tert-butylhexacetylene [3]; and phenyltriacetylene, obtained for the first time by reaction between monoiodoacetylene and phenylacetylene magnesium bromide [4]; the same hydrocarbon was later synthesized by another route: α-bromocinnamaldehyde was condensed with propargyl alcohol (2-propyn-1-ol) to the glycol which was readily transformed into the dichloride from which the triacetylene was obtained by dehydrohalogenation [5].

The following symmetrically substituted triacetylenes are known: dimethyltriacetylene (octatriyne-2,4,6) and diethyltriacetylene (decatriyne-3,5,7), obtained by the action of sodium amide on the corresponding dichlorides [6]; ditert-butyltriacetylene [3], dicyclohexenyltriacetylene [6] and diphenyltriacetylene [6–8].

In the preceding paper [9] we described a new method of preparation of branched diacetylenic hydrocarbons with a β-position of the triple bonds by propargylation of alkynes-1 magnesium bromides with tertiary acetylenic chlorides of the type of $R_2CCl-C\equiv C-R$ in presence of $HgCl_2$ and Cu_2Cl_2. The objective of the present work was to propargylate alkynes-1 magnesium bromides with ditertiary acetylenic dichlorides of the type of $R_2CCl-C\equiv C-CClR_2$. The realization of this reaction opens a route to the synthesis of previously undescribed β-triynes of the type of

$$R-C\equiv C-\underset{|}{\overset{|}{C}}-C\equiv C-\underset{|}{\overset{|}{C}}-C\equiv C-R.$$

The utilization of the above-mentioned dichlorides in organomagnesium synthesis has been reported in a number of cases in the literature. Thus, an unsuccessful attempt to synthesize an alkyne of branched structure by reaction of methyl magnesium bromide with 2,5-dichloro-2,5-dimethylhexyne-3 has been described; instead of the expected ditert-butylacetylene, however, the sole reaction product was a solid polymer [10]. A repetition of this reaction by other workers likewise gave negative results [11].

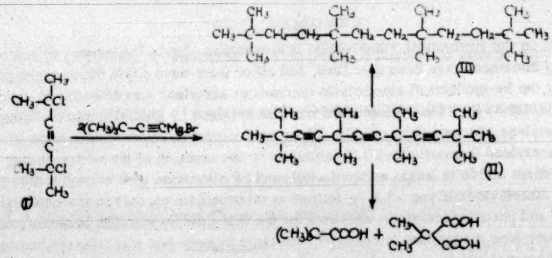
A. D. Petrov and L. N. Lavrishcheva showed that the synthesis of acetylenic hydrocarbons by such a route can be realized if acetylenic dichlorides with heavier radicals are used. Thus the authors reacted ethyl magnesium bromide with the dichloride corresponding to sym. dimethyl-ditert-butylbutynediol and obtained a monoacetylenic hydrocarbon with four quaternary carbon atoms [12].

The starting substances in the present work were tert-butylacetylene magnesium bromide and 2,5-dichloro-2,5-dimethylhexyne-3 (I), prepared by the action of concentrated hydrochloric acid on tetramethylbutynediol [13]. The catalysts used were $HgCl_2$ and Cu_2Cl_2.

The reaction gave a 60% yield (calculated on the dichloride taken) of a product with m.p. 46–47°, the elementary analysis and molecular weight determination of which pointed to the formula $C_{20}H_{30}$. Raman spectrographic examination revealed the presence of a triple bond (2229 cm^{-1}).

The structure of the hydrocarbon was verified by ozonization. Decomposition of the products of ozonolysis gave trimethylacetic and dimethylmalonic acids, thus enabling us to attribute to the hydrocarbon

the structure of 2,2,5,5,8,8,11,11-octamethyl-dodecatriyne-3,6,9 (II). The synthesized hydrocarbon is the first representative of the highly branched triacetylenes with four quaternary carbon atoms and with a β-position of the three triple bonds. Like all branched acetylenic hydrocarbons it is very stable to oxidizing agents. After heating at the boil with alkali solution of $KMnO_4$ for 48 hours, the hydrocarbon was recovered unchanged. An attempt to accomplish the oxidation in acetone was also unsuccessful. Hydrogenation of the hydrocarbon in presence of $PdCl_2$ on $CaCO_3$ caused addition of 6 molecules of hydrocarbon and a hydrocarbon $C_{20}H_{42}$ was obtained. Which, on the basis of the well-authenticated structure of the original triyne (II), must be assigned the structure of 2,2,5,5,8,8,11,11-octamethyldodecane (III).



EXPERIMENTAL

Preparation of 2,2,5,5,8,8,11,11-octamethyl-dodecatriyne-3,6,9 (II). To the Grignard reagent, prepared in the usual fashion from 25 g Mg and 119 g ethyl bromide in 650 ml ether, was added 82 g tert-butylacetylene in 100 ml ether in the course of 7 hours with continuous stirring and cooling. After standing 36 hours, the mixture was heated on a water bath until ethane ceased to come off, after which it was cooled to room temperature. To the complex tert-butylacetylene magnesium bromide was added a mixture of 2 g Cu_2Cl_2 and 1 g $HgCl_2$ as catalyst, and with cooling the dichloride (I) was added in the amount of 90 g diluted with 300 ml ether. This mixture was let stand for 36 hours; it was then heated with stirring on a water bath for 4 hours and decomposed, while cooling, with dilute hydrochloric acid. The collected ethereal solution, together with the ether extracts, was dried with calcined sodium sulfate, and the ether was driven off. Vacuum distillation of the reaction products gave two fractions: up to 82° at 14 mm the unreacted dichloride (I) came over; between 82 and 104° at 14 mm a fraction was obtained that crystallized for the most part in the condenser. The second fraction was redistilled at 0.064 mm and gave a substance with b.p. 62–64°. It crystallized completely.

M.p. 47°, d_4^{50} 0.7715, n_D^{50} 1.4295, $n_F^{50}-n_C^{50}$ 0.094; ω_{FCD} 21.9, MR_D 90.47. $C_{20}H_{30}\left|\begin{matrix}\equiv\\ 3\end{matrix}\right.$. Calc. 88.37.

Found %: C 88.01, 88.00;* H 11.09, 11.31. M 271.10, 265.18, $C_{20}H_{30}$. Calc. %: C 88.82; H 11.18. M 270.46.

The Raman spectrum of the hydrocarbon (II) was obtained with a glass spectrograph with a system of three ISP-51 constant-deviation prisms (exciting line Hg 22938 cm^{-1}), glass filter, width of slit 0.003 mm, exposure 6 hours. The procedure for plotting the Raman spectra of substances in the fused state was described in the preceding paper [9]. The intensity of the lines was evaluated visually, using a 5-step scale.

233 (1), 616 (2), 1028 (1), 1112 (1), 1210 (3), 1345 (1), 1447 (3), 2176 (1), 2206 (2), **2229** (5), 2275 (3).

Ozonization of hydrocarbon (II). 5 g hydrocarbon was ozonized in a solution of 50 ml purified chloroform until ozone ceased to be absorbed. The solvent was taken off in vacuum; the ozonide was decomposed with water, first at the ordinary temperature and then with heating on a water bath. The solution of the products

* Considerable difficulties were encountered in the elementary determination of carbon and hydrogen due to the high volatility of the compound.

of ozonization, with an acidic reaction, were treated with powdered chalk. Only traces of neutral substances were found when the products of ozonolysis were distilled with steam. The solution was then acidified with sulfuric acid. Distillation of the volatile acids from the acidic products gave trimethylacetic acid (light feathery crystals with m.p. 34–35°); also several aqueous fractions were collected of 5 ml each, heating of which with freshly prepared silver carbonate gave silver salts corresponding to trimethylacetic acid.

Found %: Ag 51.60, 51.80. $C_5H_9O_2Ag$. Calc. %: Ag 51.62.

The residue after distillation of the volatile acids was extracted with ether. Crystals of dimethylmalonic acid with m.p. 187° came down for the ethereal solution.

Found: equiv. 67.3, 67.4. M 134.6, 134.8, $C_5H_8O_4$. Calculated: equiv. 66.05. M 132.11.

The silver salt of dimethylmalonic acid was also prepared.

Found %: Ag 62.09. $C_5H_6O_4Ag_2$. Calc. %: Ag 62.38.

Oxidation of hydrocarbon (II). 1) 3 g hydrocarbon and 0.35 g potassium hydroxide in 75 ml water were placed in a round-bottomed flask with a reflux condenser. $KMnO_4$ was added in small portions at the boil. Oxidation was not observed in spite of prolonged boiling. The hydrocarbon was recovered unchanged. 2) An attempt to oxidize the compound in acetone in the cold was also unsuccessful; on boiling, the acetone was oxidized while the compound was unchanged.

Hydrogenation of hydrocarbon (II). 2 g catalyst, prepared by the method of Busch [14] ($PdCl_2$ on $CaCO_3$) in 60 ml ethyl alcohol, was saturated with hydrogen, and 2 g hydrocarbon (II) was introduced. Addition of hydrogen during the first 8 minutes went very energetically and 490 ml was taken up; the speed then fell off and a further 496 ml hydrogen was absorbed in the course of 4 hours, making 986 ml in all (the theoretical amount for three triple bonds is 994 ml). After driving off the solvent, the product of hydrogenation was recrystallized from methanol; m.p. 37–38° and with analysis corresponding to the saturated hydrocarbon (III).

Found %: C 85.20; H 14.10. M 280.1. $C_{20}H_{42}$. Calc. %: C 85.38; H 14.62. M 282.6.

SUMMARY

1. A method is proposed for the preparation of previously undescribed triacetylenic hydrocarbons with a β-position of the triple bonds by propargylation of alkynes-1 magnesium bromides with tertiary acetylenic dichlorides of the type of $R_2CCl-C\equiv C-CClR_2$.

2. Reaction of tert-butylacetylene magnesium bromide with 2,5-dichloro-2,5-dimethylhexyne-3 (I) gave the first representative of completely methylated β-triacetylenic hydrocarbons with four quaternary carbon atoms: 2,2,5,5,8,8,11,11-octamethyl-dodecatriyne-3,6,9 (II). The structure of the hydrocarbon was confirmed by preparation by ozonization of trimethylacetic and dimethylmalonic acids.

3. Exhaustive hydrogenation of hydrocarbon (II) on palladium catalyst ($PdCl_2$ on $CaCO_3$) gave 2,2,5,5,8,8,11,11-octamethyldodecane (III).

LITERATURE CITED

[1] W. Hunsmann, Ber., 83, 213 (1950).

[2] E. R. H. Jones et.al., J. Chem. Soc., 1952, 2010.

[3] F. Bohlman, Ber., 86, 657 (1953).

[4] V. Grignard, Techeou Fa-Ki, Comptes rend. 188, 359 (1929).

[5] E. R. H. Jones et.al. Nature, 168, 900, 4282 (1951).

[6] F. Bohlmann, Angew. Chem., 63, 218 (1951).

[7] H. Schlubach and V. Franzen, Ann., 572, 116 (1951); M. Nakagava, Proc. Japan Acad., 26, 43 (1950).

[8] E. R. H. Jones and Whiting, J. Chem. Soc., 1954, 147.

[9] A. I. Zakharova and G. M. Murashov, J. Gen. Chem. 25, 1453 (1955). (T.p. 1397)•

[10] G. F. Hennion and T. F. Banigan, J. Am. Chem. Soc., 68, 1202 (1946).

[11] R. Ya. Levina and Yu. S. Shabarov, Vestnik Moscow State Univ., No. 2, 77 (1953).

[12] A. D. Petrov and L. N. Lavrishcheva, Proc. Acad. Sci. USSR, 89, 313 (1953).

[13] A. I. Zakharova and I. M. Stroiman, J. Gen. Chem., 15, 438 (1945); A. I. Zakharova and G. D. Ilyina, J. Gen. Chem., 24, 2144 (1954). (T.p. 2115)•

[14] Busch and Stove, Ber., 49, 1063 (1916).

Received August 15, 1954

Leningrad State University

• T.p. = C. B. Translation pagination.

SYNTHESIS OF N^4-SULFANILAMIDE DERIVATIVES OF THE LYSINE SERIES

Yuan Chen-e and M. N. Shchukina

Trefouel, Nitti and Bovet [1] reached the conclusion, on the basis of their investigations, that the chemotherapeutic activity of sulfanilamide compounds is closely associated with the presence of a free amino group and that sulfanilamide preparations with a blocked amino group (N^4-substituted derivatives) manifest a very low therapeutic action in comparison with white streptocide. This opinion is not supported by the facts: the investigated N^4-substituted sulfanilamide compounds include a series of active preparations. Thus, for example, Septasin (N^4-benzylsulfanilamide) has found practical application; the activity of p-sulfamidophenylglycine (sulfanilamide 22) is $1\frac{1}{2}$ times higher than that of white streptocide [2].

In view of the physiological importance of the essential amino acids, we prepared a number of N^{α}-sulfanilamide derivatives of the lysine series [3]. Taking into account the high activity of p-sulfamidophenylglycine, we have also realized in the present work the synthesis of N^4-sulfanilyl-derivatives of d,l-lysine substituted at the α-and ϵ-amino groups and of α, ϵ-disubstituted lysines.

The synthesis was effected according to the scheme shown.*

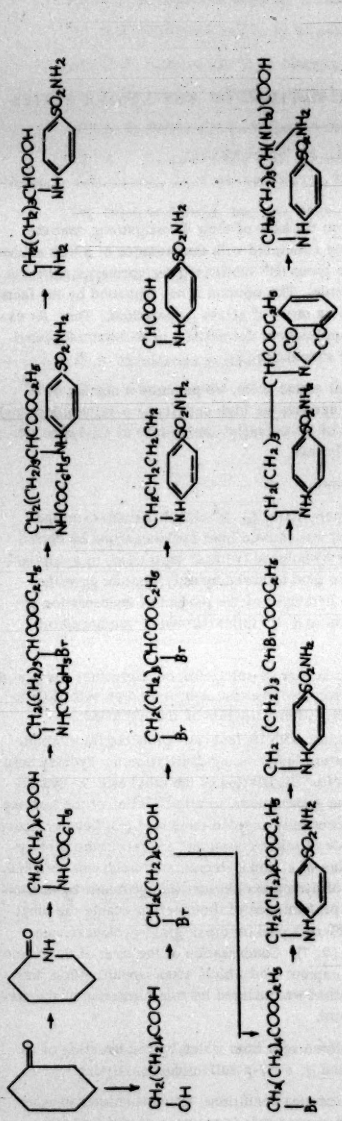
The starting substance for synthesis of α-p-sulfamidophenyllysine (α-N^4-sulfanilamido-ϵ-aminocaproic acid) was α-bromo-ϵ-benzoylaminocaproic acid, which was derived from cyclohexanone by Beckmann rearrangement of its oxime to caprolactam; the latter was hydrolyzed (without separation) to ϵ-aminocaproic acid. Bromination of the benzyl derivative of this amino acid followed by esterification gave the ethyl ester of α-bromo-ϵ-benzoylaminocaproic acid. Alkaline hydrolysis of the product of condensation of the ester of the bromo-acid with sulfanilamide leads to formation of α-N^4-sulfanilamido-ϵ-aminocaproic acid.

For preparation of ϵ-N^4-sulfanilamido-α-aminocaproic acid (ϵ-p-sulfamidophenylglycine) and α,ϵ-di-p-sulfamidophenylglycine, ϵ-bromocaproic acid was obtained from cyclohexanone by oxidation with H_2O_2 to ϵ-hydroxycaproic acid and substitution of hydroxyl by Br via HBr. After oxidation of the cyclohexanone, the ϵ-hydroxycaproic acid is isolated in the form of a mixture with its lactone. Unsuccessful attempts to separate these two compounds have been reported in the literature [4,5]; during distillation the hydroxy acid is partly lactonized and partly transformed into an unsaturated acid. Distillation of the ethyl ester ϵ-hydroxycaproic acid leads, as shown by Robinson and Smith [6] and by our experiments, to esterification of the hydroxy group of one molecule by the carboxyl group of another. We successfully avoided these side reactions by treating the crude hydroxy acid with 48% hydrobromic acid in presence of sulfuric acid and a small quantity of hydrogen peroxide. In the absence of peroxide a low-boiling mixture of ϵ-and δ-brominated acids was obtained. Since ϵ-bromocaproic acid decomposes on distillation with loss of hydrogen chloride, we purified it by distillation of its ethyl ester in vacuum. The conditions worked out for performance of the reaction enable the ethyl ester of ϵ-bromocaproic acid to be obtained in a yield of 40–42% reckoned on the original cyclohexanone (yields of 19–28% of the free acid are reported in the literature) [5, 7]. Condensation of the ester of the bromo acid with sulfanilamide gave the ethyl ester of ϵ-sulfanilamido-caproic acid which, after saponification, was brominated in a medium of phosphorus trichloride. Gabriel's method was utilized for transformation of the prepared α-bromo acid into α-amino-ϵ-N^4-sulfanilamidocaproic acid.

Bromination of ϵ-bromocaproic acid gave the α, ϵ-dibromo acid from which, by condensation of its ester with excess sulfanilamide in presence of catalyst, was obtained α, ϵ-di-p-sulfamidophenyllysine.

Several authors have found [8] that depending upon the reaction conditions, sulfamilamide can react with halo derivatives either at the amino or the amido group. We showed that in presence of pyridine and potassium iodide the condensation takes place at the amino group and proceeds with a considerably higher yield than without a catalyst. Condensation of sulfanilamide with the ester of α, ϵ dibromocaproic acid demands more drastic conditions with use of a copper salt as catalyst.

* See following page.



EXPERIMENTAL

ε-Benzoylaminocaproicacid. The oxime was prepared from cyclohexanone by the method of Eck and Marvel [9]. Rearrangement of the oxime was effected in small portions in view of the violet reaction. The caprolactam formed was not isolated but was directly subjected to hydrolysis. After Schotten-Baumann benzoylation, ε-benzoylaminocaproic acid was separated in the form of a white crystalline substance melting at 78–80°. Yield 73% reckoned on the oxime.

Ethyl ester of ε-benzoylamino-α-bromocaproic acid. ε-Benzoylaminocaproic acid was brominated by the literature method [10]. The resultant bromo acid (93% yield) (20 g, m.p. 162.5–165°) was esterified in the usual manner in presence of sulfuric acid. The resultant transparent oil crystallized in the course of a day when cooled to −10°. Yield 17.3 g (80%). After recrystallization from 8 times the volume of ligroine, ethyl-benzoylamido-α-bromocaproate was obtained with m.p. 56–57°.

Found %: N 4.10; Br 23.38. $C_{15}H_{20}O_3NBr$ Calc. %: N 4.09; Br 23.39.

α-N^4-sulfanilamido-ε-aminocaproic acid. A mixture of 6.84 g ethyl α-bromo-ε-benzoylaminocaproate, 6.88 g sulfanilamide and 0.3 g potassium iodide in 40 ml anhydrous alcohol was heated in a sealed glass tube at 140–160° for 14 hours. After cooling, 2.9 g unreacted sulfanilamide was recovered. The alcoholic solution was evaporated to dryness and the residual oil washed with 10% hydrochloric acid (twice with 15 ml lots of acid) and water. The oil (non-crystallizing when intensely cooled) did not give a positive test for halogen; it was saponified by heating with 60 ml 10% KOH at 85–90° for 5 hours. Acidification with hydrochloric acid (to congo) gave 1.9 g benzoic acid. The filtrate was extracted with ether and the aqueous layer evaporated to dryness. The residue was extracted with 2% hydrochloric acid. After neutralization of the acid solution with ammonia (litmus test), α-N^4-sulfanilamido-ε-aminocaproic acid was isolated; after recrystallization from water (1:5) it melted at 200–201°. Yield 4.32 g (72%). For analysis it was recrystallized twice from water. Colorless needles with m.p. 202°, soluble in water and alcohol, almost insoluble in other common organic solvents.

Found%: N 13.83; S 10.71. $C_{12}H_{19}O_4N_3S$. Calc. %: N 14.00; S 10.63.

Ethyl ε-bromocaproate. To 110 ml 20% NaOH was added at 50 ± 5° simultaneously from two separating funnels 50 g cyclohexanone (b.p. 153–156°) and 185 ml

hydrogen peroxide (26%) with stirring in the course of 45 minutes. Oxidation takes place exothermically with evolution of hydrogen; the reaction temperature was controlled by cooling with cold water. After addition of the reactants, stirring was continued for a further 1½ hours at room temperature. The reaction mass was twice extracted with ether (40 ml each time) for removal of unreacted cyclohexanone, after which the aqueous alkaline solution was acidified with concentrated hydrochloric acid to congo (50 ml). Addition of ammonium sulfate to the acid solution brought down the hydroxy acid in the form of an oily layer. The aqueous layer was extracted with ether (twice with 50 ml each time) and the ether extract was combined with the oily substance and, after cooling, treated with sodium sulfate. The ether extract, freed in this manner form peroxides (starch-iodide test), was dried over sodium sulfate and evaporated to dryness; the syrupy residue (45–50 g) was soluble in bicarbonate solution. It was dissolved in 140 ml 48% hydrobromic acid and gradual addition was made, with stirring, of 35 ml concentrated sulfuric acid and 5 ml 26% hydrogen peroxide. The orange solution was stirred at first at room temperature (2 hours) and then on a boiling water bath for 5 hours. The acidic solution (separated from the resin formed) was diluted with 500 ml water and 250 g ammonium sulfate was added. The solution was extracted with ether. The ether extract was dried with sodium sulfate and evaporated to leave a residue of dark-red oil which was converted to the ethyl ester in the usual manner in presence of sulfuric acid. The ethyl ε-bromocaproate was fractionally distilled in vacuum. The 100–105° (1.2 mm) fraction was collected. Yield 48 g (42%, reckoned on the cyclohexanone).

Found %: Br 35.26, 35.38. $C_8H_{15}O_2Br$. Calc. %: Br 35.87.

Considerable decomposition with loss of hydrogen bromide was observed during distillation of the free ε-bromo acid. The 145–170° (0.8 mm) fraction crystallized when cooled with freezing mixture. After recrystallization from ligroine the acid had m.p. 33–34°, in agreement with the literature data [7] for ε-bromocaproic acid. The acid can be recrystallized from 10% hydrochloric acid.

Ethyl ester of ε-N^4-sulfanilamidocaproic acid. A mixture of 5.58 g ethyl ε-bromocaproate, 4.3 g sulfanilamide, 1 g potassium iodide and 2.2 g pyridine in 30 ml anhydrous alcohol was heated 21 hours on a water bath at the boiling point of the alcohol. The solution was then evaporated to dryness and the residue washed successively with 25 ml water, 20 ml ether, 10 ml 5% sodium carbonate, and again with water. The solid substance was twice recrystallized from 50% alcohol. The ethyl ester of ε-N^4-sulfanilamido-caproic acid is a white crystalline powder with m.p. 95–96°, insoluble in water and ether, readily soluble in hot alcohol and poorly soluble in cold alcohol. Yield 4.7 g (60%).

Under the same conditions but without potassium iodide the yield was only 25–30%.

Found %: C 53.45; H 6.99; N 8.85, 8.73. $C_{14}H_{22}O_4N_2S$. Calc. %: C 53.50; H 7.01; N 8.91.

ε-N^4-Sulfanilamido-caproic acid. A mixture of 2.1 g ethyl ester of ε-N^4-sulfanilamido-caproic acid and 9 ml 10% potassium hydroxide was heated at the boil for 3 hours. The hot solution was treated with carbon and the filtrate acidified with 20% hydrochloric acid (to congo). An oil separated which crystallized when rubbed. Recrystallization from water (50 ml) gave 1.55 g (81%) ε-N^4-sulfanilamido-caproic acid. Lustrous crystals with m.p. 126–126.5°, insoluble in benzene and chloroform, poorly soluble in cold water, readily soluble in caustic alkalies. Like N^4-sulfanilamido-acetic acid (sulfoglycine), this compound gives a diazo-coupling reaction with β-naphthol.

Found %: N 9.62; S 11.42, 10.92. $C_{12}H_{18}O_4N_2S$. Calc. %: N 9.79; S 11.19.

α-Bromo-ε-N^4-sulfanilamido-caproic acid. To a suspension of 3.65 g ε-N^4-sulfanilamidocaproic acid in 75 ml phosphorus trichloride with intensive stirring was added 8 g (2.2 ml) bromine dried over sulfuric acid. The mixture was boiled on a water bath for 10 hours; the excess phosphorus trichloride was then distilled off and the residue decomposed with iced water (150 ml). The dark-brown precipitate was washed with water, dried in a vacuum-disiccator and dissolved in alcohol. The alcoholic solution was treated with carbon, filtered and run into water to give a white precipitate of ε-N^4-sulfanilamido-α-bromocaproic acid, m.p. 150–152° (from 50% alcohol). Yield 3.45 g (74%).

Found %: N 7.70, 7.59; Br 21.73. $C_{12}H_{17}O_4N_2SBr$. Calc. %: N 7.67; Br 21.92.

α-Amino-N^4-sulfanilamidocaproic acid. The prepared α-bromo-ε-N^4-sulfanilamido-n-caproic acid was converted into the ester in 82% yield by the usual method. A mixture of 3.5 g of the ethyl ester of α-bromo-ε-N^4-sulfanilamidocaproic acid and 1.65 g potassium phthalimide was heated at 140–150° on an oil bath for

30 minutes. The reaction mixture was then run into a dish and, after cooling, was dissolved in boiling 50% alcohol. There was obtained 3.7 g of the ester of α-phthalimido-ε-N^4-sulfanilamido-n-caproic acid which was saponified by boiling with 9 ml 10% KOH (1:2). After cooling, the solution was treated with concentrated hydrochloric acid until the alkaline reaction (to phenolphthalein) had disappeared. The separated α-phthalimido-ε-N^4-sulfanilamido-n-caproic acid was refluxed with 10 ml 20% HCl while stirring. After 2 hours boiling, phthalic acid (1.1 g) separated from the solution. The acid solution was evaporated to dryness in vacuum; the solid residue was washed with anhydrous alcohol (twice with 5 ml each time) and then dissolved in water. Addition of sodium acetate to the saturated aqueous solution of the hydrochloride of α-amino-ε-N^4-sulfanilamido-caproic acid until the acid reaction (to congo) had disappeared led to separation of a crystalline substance which after two recrystallizations from 50% alcohol melted at 186–187°. Yield 1.3 g (51%, reckoned on the original α-bromo-ε-N^4-sulfanilamido-caproic acid). The prepared ε-N^4-p-sulfamidophyl-d, l-lysine is poorly soluble in water, readily soluble in alcohol and inorganic acids and caustic alkalies. It gives a blue coloration with sodium nitroprusside.

Found %: N 13.82; S 10.61. $C_{12}H_{19}O_4N_3S$. Calc. %: N 14.00; S 10.63.

Ethyl α, ε-dibromocaproate. To a solution of 6.3 g ε-bromocaproic acid (m.p. 35°) in 10 ml phosphorus trichloride was added dropwise 7.5 g (2.5 ml) dry bromine, and the reaction mass was stirred for 30 minutes at room temperature, after which it was refluxed on a water bath for 7 hours (5 hours at 70–80° and 2 hours at 95–98°). The mass thickened on cooling and the following day it was run into 150 ml alcohol. The oily product obtained by evaporation of the alcoholic solution in vacuum was washed with sodium bicarbonate solution and water at a temperature not above 5°, dissolved in ether, and dried with sodium sulfate. Ethyl α, ε-dibromocaproate was distilled in vacuum at 128–130° (1.5 mm). Yield 6.73 g (76%).

Found %: Br 52.69. $C_8H_{14}O_2Br_2$. Calc. %: Br 52.98.

α, ε-Bis-N^4-sulfanilamido-caproic acid (di-N-p-sulfamidophenyl-d, l-lysine). A mixture of 5.5 g ethyl α, ε-dibromocaproate, 6.9 g sulfanilamide, 2.5 pyridine and 2 g copper acetate in 40 ml anhydrous alcohol was heated in a sealed tube at 160–180° for 20 hours. The alcoholic solution was evaporated to dryness in vacuum and the residue washed with 10% hydrochloric acid (two lots of 10 ml) and with water. The product was saponified by heating with 15 ml 10% KOH. Hydrogen sulfide was passed through the alkaline filtrate to bring down the copper. Acidification with concentrated hydrochloric acid (to congo) of the solution (decolorized with carbon) brought down a white precipitate. After two recrystallizations form 75% alcohol, di-N-p-sulfamidophenyl-d, l-lysine forms colorless needles with m.p. 227–229°. Good solubility in alcohol, poor in water.

Found %: C 47.57; H 5.28; N 12.58, 12.03. $C_{18}H_{24}O_8N_4S_2$. Calc. %: C 47.37; H 5.26; N 12.28.

SUMMARY

1. α- and ε-mono- and α, ε-bis-N^4-sulfanilamido derivatives of the d,l-lysine series were synthesized.

2. ε-N^4-sulfanilamido-caproic acid and its ester were prepared.

3. It was found that condensation of sulfanilamide through the amino group with an ester of α-bromo-ε-benzoylaminocaproic acid and with an ester of ε-bromocaproic acid proceeds with better yield in presence of potassium iodide and pyridine, while the presence of a copper salt is necessary for condensation of sulfanilamide with ethyl α, ε-dibromocaproate.

4. A method was devised for the preparation of ethyl ε-bromocaproate.

LITERATURE CITED

[1] J. Trefouel, F. Nitti and D. Bovet, Ann. Inst. Pasteur, 58, 30 (1937).

[2] M. V. Rubtsov, J. Gen. Chem., 10, 831 (1940).

[3] M. N. Shchukina and Yuan Chen-e, J. Gen. Chem., 24, 687 (1954). (T.p. 695)

[4] Helferich and Malkomes, Ber., 55B, 702 (1922); C. S. Marvel and MacCorcuodale, J. Am. Chem. Soc., 46, 2838 (1924).

[5] Fox and Polak, J. Am. Chem. Soc., 73, 4979 (1951).

[6] Robert Robinson and L. H. Smith, J. Chem. Soc., 1937, 371.

[7] H. W. Heine and H. Jones, J. Am. Chem. Soc., 73, 1361 (1951).

[8] Montague and A. Phillips, J. Chem. Soc., 1941, 9; Schroeter, Z. angew. Chem., 39, 1460 (1926); Johnson and McCollum, J. Am. Chem., 35, 58 (1906).

[9] J. Eck, C. Marvel, J. Biol. Chem., 106, 387 (1934).

[10] Organic Synthesis, Col. V., 2, 74 (1946).

Received November 1, 1954

S. Ordzhonikidze Scientific Research
Institute of Pharmaceutical Chemistry

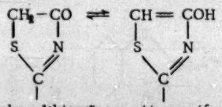
• T.p. = C. B. Translation pagination.

4-KETOTHIAZOLES (4-HYDROXYTHIAZOLES)

II. REACTIONS OF THE METHYLENE GROUP OF 2-PHENYLTHIAZOLINONE-4

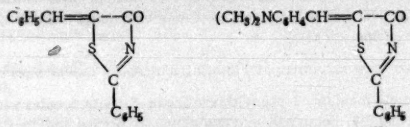
F. N. Stepanov and Z. Z. Moiseeva

Recently we described [1] the synthesis of 2-phenylthiazolinone-4. The system of thiazolinone-4 is tautomeric with the system of 4-hydroxythiazole:



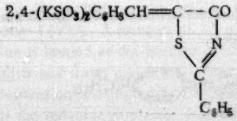
The phenolic character of 2-phenylthiazolinone-4 is manifested by the weakly acidic properties and by the tendency to form acyl derivatives. However its most characteristic features are reactions of the methylene group. This communication is devoted to these reactions.

In presence of concentrated sulfuric acid 2-phenylthiazolinone-4 readily enters into condensation with benzaldehyde to form the benzylidene derivative (I). The p-dimethylaminobenzylidene derivative (II) is similarly formed. In alkaline, aqueous solution 2-phenylthiazolinone-4 condenses with benzaldehyde-2,4-disulfonic acid to form a disulfobenzylidene derivative which is isolated in the form of a nicely crystallizing potassium salt (III).

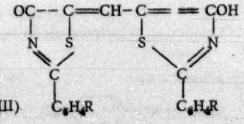


(I)

(II)



(III)



(IV) R = H;

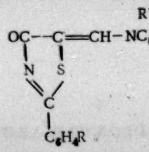
(V) R = p-NO_2

The simplest methine dye of the 2-phenylthiazolinone-4 series is bis-(2-phenylthiazolinone-4)-5,5'-methine (IV).

The dye is prepared from 2-phenylthiazolinone-4 and ethyl orthoformate by boiling in pyridine solution, and it crystallizes from glacial acetic acid in the form of fine, small purple needles. The purple alcoholic solution of the dye turns blue when made alkaline and turns yellow when acid. Formation of a similar dye from 2-ethylmercaptothiazolinone-5 and ethyl orthoformate has been reported [2].

Dye (IV) is also formed by condensation of 2-phenylthiazolinone-4 with diphenylformamidine on boiling in pyridine solution. At the same time 2-phenyl-5-anilinomethylenethiazolinone-4 (VI) is formed; this crystallizes from butanol as a yellow, finely crystalline powder.

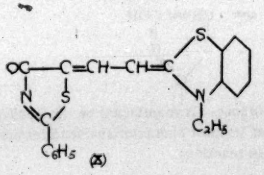
Condensation of 2-(4-nitrophenyl)-thiazolinone-4 with diphenylformamidine also leads to two compounds; the methine dye (V) – dark-blue needles from pyridine, m.p. 272–273°, and the anilinomethylene derivative (VII) – orange-red plates from pyridine, m.p. 309–310°.



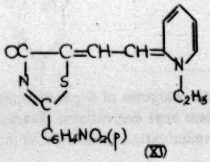
(VI) R═H, R'═H;
(VII) R═NO_2, R'═H;
(VIII) R═H, R'═CH_3CO
(IX) R═NO_2, R'═CH_3CO.

The anilinomethylene derivatives (VI) and (VII) are acetylated on boiling in acetic anhydride, forming 2-phenyl-5-acetoanilinomethylenethiazolinone-4 (VIII) (yellow, finely crystalline powder, m.p. 201–202°) and 2-(4-nitrophenyl)-5-acetanilinomethylenethiazolinone-4 (IX) (orange plates, m.p. 277–278°).

From the acetoanilino derivatives we can pass to the merocyanine dyes of the phenylthiazolinone-4 series. This is exemplified by the preparation of (2-phenyl-4-keto-4,5-dihydrothiazole-5)-dimethine-(3-ethylbenzothiazole-5) (X). The dye is obtained by condensation of (VIII) with 2-methylbenzothiazole methoiodide in isopropyl alcohol in presence of triethylamine.



(X)



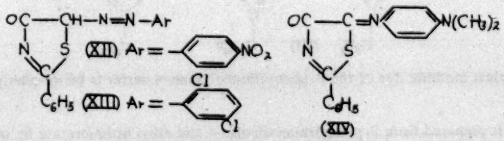
(XI)

It has an absorption maximum (in alcohol) of 568 mμ and it weakly sensitizes silver bromide emulsion in the yellow-green region of the spectrum. Another example of the preparation of a merocyanine dye of this series is the condensation under similar conditions of 2-(4'-nitrophenyl)-thiazolinone-4 with 2-β-acetanilinovinylpyridine ethoiodide, leading to formation of (2-p-nitro-phenyl-4-keto-4,5-dihydrothiazole-5)-dimethine-(1-ethyl-1,2-dihydropyridine-2) (XI).

This dye, absorption maximum at 576 mμ (in alcohol), desensitizes silver bromide emulsion.

In an acetic acid medium, 2-phenylthiazolinone-4 easily couples with diazo compounds: with 4-nitrophenyldiazonium and 2,5-dichlorophenyldiazonium, the orange-red dyes (XII) and (XIII) whose color changes to blue in an alkaline medium, are found.

A last example of a reaction of the methylene group of 2-phenylthiazolinone-4 is the formation of the azomethine dye (XIV) by condensation with nitrosodimethylaniline.



(XII) Ar═ NO_2
(XIII) Ar═ Cl, Cl
(XIV)

EXPERIMENTAL

2-Phenyl-5-benzylidenethiazolinone-4 (I). 3 ml sulfuric acid is added dropwise, with stirring, to a mixture of 0.5 g 2-phenylthiazolinone-4, 0.3 g benzaldehyde and 10 ml alcohol. With cooling, the bright-yellow solution is poured on to 50 g ice; the precipitate is filtered, washed with water and dried. The compound (0.8 g, m.p. 105–110°) is dissolved in ether and filtered, and the ether is evaporated. The residue is crystallized from gasoline to give 0.4 g (53%) yellow substance, m.p. 129–130°.

Found %: N 5.34, 5.42. $C_{16}H_{11}ONS$. Calc. %: N 5.28.

2-Phenyl-5-(p-dimethylaminobenzylidene)-thiazolinone-4. 2 ml concentrated sulphuric acid is introduced dropwise with stirring into a mixture of 0.2 g 2-phenylthiazolinone-4, 0.2 g 4-dimethylaminobenzaldehyde and 5 ml alcohol. The olive-colored solution is poured (with cooling) on to 50 g ice. The precipitate is filtered, washed with water and dried. The compound (0.25 g, 96–106°) is extracted with ether; the ether is evaporated and the residue crystallized from glacial acetic acid. Fine brown needles, m.p. 120–122°. Yield 0.18 g (51%).

Found %: N 9.00, 8.90. $C_{18}H_{16}ON_2S$. Calc. %: N 9.09.

2-Phenyl-5-(benzylidenedisulfonic acid-2',4')-thiazolinone-4 (III). A filtered solution of 2 g 2-phenylthiazolinone-4 in 200 ml water and 4 ml 40% sodium hydroxide is added, at 10° over a period of 45 minutes, to a solution of 3.5 g sodium salt of benzaldehyde-2,4-disulfonic acid in 18 ml water and 6 ml hydrochloric acid (d 1.16). The solution (neutral reaction) is heated for 20 minutes at 80° and filtered hot; 5 g potassium chloride is added, and the solution is run (with cooling) into 30 ml alcohol. The precipitate is filtered, washed with alcohol and crystallized from water. White, lustrous needles; weight 3.3 g (58.5%).

Found %: S 19.26, 19.20. $C_{16}H_9O_7NS_3K_2$. Calc. %: S 19.30.

Bis-(2-phenylthiazolinone-4)-5,5'-methine (IV). A solution of 1 g 2-phenylthiazolinone-4 and 0.42 g ethyl orthoformate in 15 ml pyridine is heated at the boil for 45 minutes. The cooled solution is run into 45 ml water and acidified with hydrochloric acid (congo test). The precipitate is collected, washed and dried. Yield 0.7 g (68%), m.p. 262–264°. Fine purple needles (from glacial acetic acid), m.p. 264–265°.

Found %: C 62.40, 62.52; H 3.58, 3.48; S 17.44, 17.64; N 8.05, 7.88. $C_{19}H_{12}O_2N_2S_2$. Calc. %: C 62.61; H 3.33; S 17.59; N 7.69.

2-Phenyl-5-anilinomethylene-thiazolinone-4 (VI). 1.3 g 2-phenylthiazolinone-4, 0.98 g diphenylformamidine and 15 ml pyridine are boiled 15 minutes. The cooled solution is diluted with 100 ml water and acidified with hydrochloric acid (congo test). The precipitate is filtered, washed with water and dried. Weight of mixture of (VI) and (IV) 1.2 g, m.p. 180–185°. The components are separated by treatment with hot isopropyl alcohol. The substance going into solution and crystallizing on cooling is the anilinomethylene derivative (VI); after recrystallization from butanol it weighs 0.3 g (15%) and has m.p. 209–210°.

Found %: C 68.33, 68.64; H 4.40, 4.37; S 11.88, 11.43; N 10.30, 10.05. $C_{16}H_{12}ON_2S$. Calc. %: C 68.54; H 4.33; S 11.43; N 9.99.

The residue insoluble in isopropyl alcohol was recrystallized from glacial acetic acid; weight 0.5 g, m.p. 264–265°; it is identical with (IV). A mixed sample with (IV) melts at 264–265°.

Bis-(2-p-nitrophenylthiazolinone-4)-5,5'-methine (V) and 2-(p-nitrophenyl)-5-anilinomethylene-thiazolinone-4 (VII). A mixture of 1.7 g 2-p-nitrophenylthiazolinone-4, 0.98 g diphenylformamidine and 10 ml pyridine is heated at the boil for 15 minutes. A precipitate comes down on cooling and is filtered, washed with pyridine and water and dried. Under the microscope the precipitate is a mixture of blue needles and red plates. Separation is effected by fractional crystallization from pyridine. The more soluble component of the mixture is the red-orange plates, m.p. 309–310°. It is (VII) and the yield is 0.2 g (8.5%).

Found %: C 59.20, 59.36; H 3.68, 3.80; S 9.70, 9.64; N 12.76. $C_{16}H_{11}O_3N_3S$. Calc. %: C 59.06; H 3.41; S 9.85; N 12.92.

The component less soluble in pyridine forms dark-blue needles with m.p. 272–273°; it is the methine dye (V); weight 0.8 g (40%).

Found %: N 12.23, 12.42; S 14.33. $C_{19}H_{10}O_4N_4S_2$. Calc. %: N 12.36; S 14.14.

Acetylation of anilinomethylene bases. 1) 0.2 g (VI) is heated with 2 ml acetic anhydride at 120° for 1 hour. Compound (VIII) comes down on cooling; a yellow granular powder, m.p. 201–202°. Yield 0.2 g (87%).

Found %: C 67.10, 67.14; H 4.42, 4.33; S 9.71; N 8.62. $C_{18}H_{14}O_2N_2S$. Calc. %: C 67.06; H 4.38; S 9.94; N 8.69.

2) Under the same conditions the acetyl derivative (X) is obtained. Orange plates from acetic anhydride, m.p. 277–278°.

Found %: N 11.24, 11.39. $C_{18}H_{13}O_4N_3S$. Calc. %: N 11.44.

Merocyanine dyes. 1) A mixture of 0.2 g (VIII), 0.2 g 2-methylbenzothiazole ethoiodide, 5 drops triethylamine and 5 ml isopropyl alcohol is boiled 6 hours. The dye (X) comes down on cooling and is filtered. Yield 0.18 g (80%). Dark-green, bronzing needles, m.p. 258° (with decomp.). Absorption maximum 568 mμ (in alcohol).

Found %: C 65.94; H 4.61; S 17.38; N 7.62. $C_{28}H_{18}ON_2S_2$. Calc. %: C 65.90; H 4.43; S 17.59; N 7.69.

2) A mixture of 0.39 g 2-β-acetylanilinovinylpyridine ethoiodide, 0.22 g 2-p-nitrophenylthiazolinone-4, 0.14 g triethylamine and 5 ml ethanol is heated on a water bath for 2 hours. Dye (XI) comes down on cooling; weight 0.2 g (56%). Dark-blue, acicular prisms, m.p. 278–279°. Absorption maximum 576 mμ (in alcohol).

Found %: N 11.70; S 9.00. $C_{18}H_{15}O_3N_3S$. Calc. %: N 11.90; S 9.07.

Azo dyes. 1) A solution of 1 g 2-phenylthiazolinone-4 in 60 ml water and 2 ml 40% sodium hydroxide is added at the same time as a solution (20 ml) of the diazonium salt from 0.81 g p-nitroaniline to a solution of 5 g sodium acetate in 30 ml water. The precipitated dye (XII) weighs 1.2 g (65%). Fine, orange needles (from xylene), not melting at above 360°.

Found %: N 17.17. $C_{15}H_{10}O_3N_4S$. Calc. %: N 17.18.

2) A dye was similarly prepared from 0.25 g 2-phenylthiazolinone-4 and 0.22 g 2,5-dichloroaniline. Yield 0.4 g (81%). Small, brown needles (from toluene), m.p. 240–242°.

Found %: S 8.79, 8.88. $C_{15}H_9ON_3SCl_2$. Calc. %: S 9.15.

Azomethine dye. To a suspension of 0.4 g 2-phenylthiazolinone-4 in 5 ml water is added an alkaline solution (about 5 ml) of p-nitrosodimethylaniline prepared from 0.3 g dimethylaniline; the mixture is left for 7 days at room temperature. The dye (XIV) is filtered and crystallized from glacial acetic acid. Yield 0.4 g (57%). Brown powder, m.p. 140–142°.

Found %: N 13.31, 13.28. $C_{17}H_{15}ON_3S$. Calc. %: N 13.59.

SUMMARY

The great mobility of the hydrogen of the methylene group of 2-phenylthiazolinone-4 is illustrated by examples of condensation with aromatic aldehydes and the preparation of methine, merocyanine and other dyes.

LITERATURE CITED

[1] F. N. Stepanov and Z. Z. Moiseeva, J. Gen. Chem., 25, 1170 (1955). (T.p. 1121)•

[2] A. Cook, G. Harries, G. Shaw, J. Chem. Soc., 1949, 1435.

Received September 17, 1954

K. E. Voroshilov Research Institute of Organic Intermediates and Dyes

• T.p. = C. B. Translation pagination.

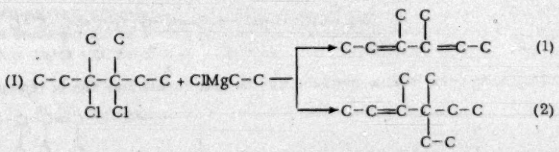
THE CONDENSATION OF PINACOL-DIHYDROGEN HALIDE REACTION PRODUCTS WITH ALLYL CHLORIDE IN PRESENCE OF MAGNESIUM

A. D. Petrov and M. P. Shebanova

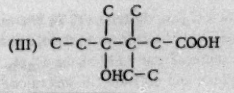
Hydrocarbons with two adjacent quaternary carbons, particularly those compounds with these carbons in the center of the molecule, are of considerable interest. Hydrocarbons of this type are characterized by high specific gravities and by an asymmetric structure and low melting point. However, the synthesis of even relatively low-molecular (C_9–C_{11}) hydrocarbons of this type has been associated with serious difficulties and it has only been accomplished with very poor yields.

Marker and Oakwood [1] obtained hexamethylethane from tert-butylmagnesium chloride and tert-butyl chloride in a yield of only 16% even in presence of CuI. In the absence of the latter the yield was only 3%, while with tertamyl chloride the yield of the corresponding isodecane was less than 1%. A higher yield of hexamethylethane [2] was got by condensation of tert-alkyl magnesium halide with a primary halide. Lengthy condensation (week) raised the yield to as much as 48%.* But even under such conditions the yield rapidly dropped with increasing length of the primary alkyl magnesium halide. In the case of ethylmagnesium bromide the yield was 22% [3], but in that of butylmagnesium bromide it was only 4% [4].

Faced with the problem of synthesizing hydrocarbons of the type in question containing C_{11}–C_{13}, we turned to other possible schemes of synthesis, and in particular we decided to study the condensation of pinacone dihalohydrins with alkyl halides and halides of the allyl type in presence of magnesium. In a first, recently published, investigation [5] we performed the condensation of the pinacone dihalohydrin obtained from methyl-ethyl ketone with ethyl magnesium chloride and with allyl chloride in presence of magnesium. Condensation was carried out at 10–15°. In the first case 3,4-dimethyl-3,4-dichlorohexane reacted mainly according to equation 1 of scheme (I), while in the second case it reacted according to scheme (II):

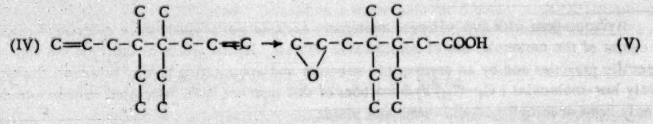


In this manner, by using an alkenyl halide with a β-position of the double bond we succeeded in obtaining a high yield of hydrocarbon in the condensation reaction, but the product contained only one quaternary carbon atom. The second atom of chlorine was simultaneously split off as HCl. It is interesting to note that the allyl rearrangement does not take place here, as was confirmed by formation of the hydroxy acid (III) on oxidation.



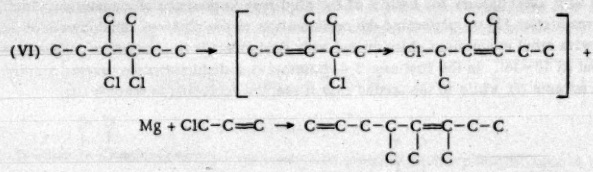
* Translator's note: got by interaction of 2,3,3-trimethyl-2-chlorobutane with methylmagnesium chloride.

In the present investigation we have continued our attempts to realize the synthesis of hydrocarbons with two adjacent quaternary carbons. We tried two routes: a) changes in the structure of the pinacol - dihydrogen halide reaction products; b) lowering of the temperature of synthesis in the hope of minimizing the secondary reaction of dehydrohalogenation. It was found, however, that the dihydrogen halide reaction products of all the pinacol taken by us (dipropyl ketone, methylisobutyl ketone, pinacoline) were inferior in stability to 3,4-dimethyl-3,4-dichlorohexane; we shall therefore not give details of the condensation of these dihydrogen halide reaction products with allyl chloride in presence of magnesium, but we shall go on to describe the condensation of alkenyl halide with 3,4-dimethyl-3,4-dichlorohexane at −20° in presence of Mg. At this low temperature we finally succeeded in obtaining a hydrocarbon with two quaternary carbons of the desired structure (IV), judging by the results of oxidation in which a C_{13} epoxy acid (acid-oxide) was obtained with the proposed structure of (V):

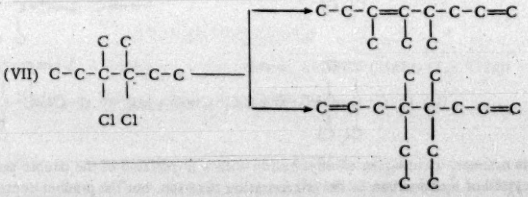


Even under these conditions, however, there was obtained, in addition to the hydrocarbon with two quaternary carbons (IV), a C_{11} hydrocarbon but with a structure different from that of C_{11} hydrocarbon obtained according to scheme (II) at 15°. Among the products of oxidation of this second hydrocarbon were found formic acid, methylethyl ketone and a C_6 ketoacid with the proposed structure C−CO−C−C−COOH, which was determined as its silver salt.

These products of oxidation indicate that at the specified low temperature of formation of the C_{11} hydrocarbon, the latter undergoes the allyl rearrangement which leads to 4,5,6-trimethyloctadiene-1,5 (scheme VI):



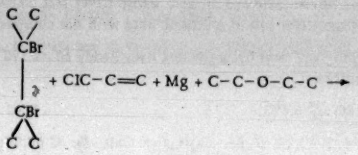
The condensation reaction proceeding at low temperature may thus be represented by scheme (VII):



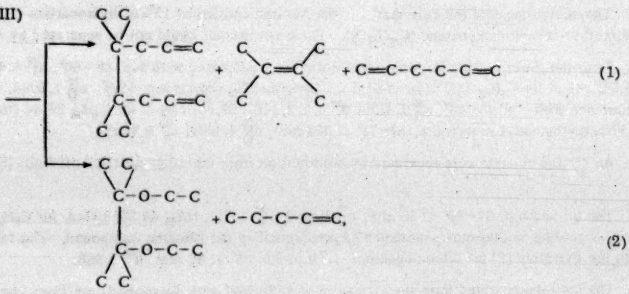
Interesting results were obtained in condensation at −20° of allyl chloride with the product of reaction with HBr of the pinacol from acetone in presence of magnesium. It was found that the reaction here proceeds according to equations 1 and 2 of scheme (VIII).

In the 145−147° fraction were found a $C_{12}H_{22}$ diolefin (12%) and a diether with the composition $C_{10}H_{22}O_2$ (88%). On increasing the amount of allyl chloride to an 8-fold excess, the formation of $C_{10}H_{22}O_2$ could be suppressed but this measure did not increase the yield of the $C_{11}H_{21}$ hydrocarbon. The main products of reaction in this case were tetramethylethylene and diallyl (1,5-hexadione). Consequently the character of

the reaction of condensation of pinacol-dihydrogen halide reaction products with Grignard reagents is governed by the structure of both components and their ratio, by the nature of the halide and by the temperature of synthesis; the reaction can therefore be varied within wide limits.



(VIII)



(1)

(2)

EXPERIMENTAL

4,5,6-Trimethyloctadiene-1,5 and 4,5-dimethyl-4,5-diethyloctane 100 g 3,4-dimethyl-3,4-dichlorohexane, prepared under the previously described conditions [5], and 152 g allyl chloride dissolved in ether were run dropwise into 48 g magnesium. At the start the mixture with a small quantity of chlorides was heated to the boiling point of ether; but when the reaction had started, the water bath was replaced by an acetone bath in which the temperature was held at −20° throughout the whole period of reaction (addition of the reaction mixture). After decomposition of the reaction mixture with NH_4Cl solution and distillation of the ether, the product with b.p. above 150° was distilled over metallic sodium. Two fractions were isolated by fractionation:

1st, b.p. 178−180° at 760 mm, n_D^{20} 1.4560, d_4^{20} 0.802, yield 38%; 2nd, b.p. 210−215° at 760 mm, n_D^{20} 1.4620, d_4^{20} 0.818, yield 10%.

By oxidation with 1% $KMnO_4$ solution the 1st fraction yielded a ketone through its 2,4-dinitrophenylhydrazone (m.p. 111°). A mixed test with the 2,4-dinitrophenylhydrazone of methylethylketone did not give a depression. Among the acidic products of reaction were identified formic acid and an acid containing 46.15 and 45.98% Ag in its silver salt. The silver salt of the anticipated ketoacid $CH_3-CO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH$ contains 45.57% Ag.

Oxidation with 1% $KMnO_4$ solution of the 2nd fraction gave only acidic oxidation products. The latter included formic acid and an acid whose silver salt contained 31.30 and 31.82% Ag.

For a dibasic acid with the composition $C_{12}H_{20}O_4Ag_2$ the content of Ag is 48.65%. For an acid oxide of the composition $C_{13}H_{23}O_3Ag$ the content of Ag is 32.2%.

The 2nd fraction was subjected to hydrogenation over Raney-Ni at 190° and 200 atm. The hydride had a b.p. 216−218°, the solidification point was below −80°, n_D^{20} 1.4440, d_4^{20} 0.798, MR_D 66.20; Calc. 66.85.

4,4,5,5-Tetramethyloctadiene-1,7 and 2,3-dimethyl-2,3-diethoxybutane 2,3-Dimethyl-2,3-dibromobutane, crystals with m.p. 168−169° (with decomp.), were obtained by passing gaseous HBr into pinacone hydrate. Stepanov analysis showed that a dibromo derivative of 99.98% purity was formed under these sonditions.

The dibromo compound was condensed at −20° with 200% excess of allyl chloride in presence of magnesium (Yavorsky's reaction) in an ether medium. Fractionation after removal of the ether gave a main fraction with b.p. 145−147°, n_D^{20} 1.4390, d_4^{20} 0.845, which decolorized bromine. 6 g of the fraction was oxidized with 1% $KMnO_4$ solution; only a small proportion of the fraction underwent oxidation. Oxidation gave only acidic products, among which were found formic acid and an acid whose silver salt contained 51.35% Ag. It was calculated that the Ag content of the silver salt of a dibasic acid with the composition $C_{10}H_{18}O_4$ is 51.92%.

The fraction with b.p. 145−147° was hydrogenated over Raney Ni at 170° and a pressure of 165 atm; it then had the following characteristics:

B.p. 148−149°, n_D^{20} 1.4180, d_4^{20} 0.823.

Found %: C 70.81, 70.84; H 13.74, 13.65. $C_{10}H_{22}O_2$. Calc. %: C 68.96; H 12.64.

The analytical data indicate that the fraction consists of 12% of hydrocarbon $C_{12}H_{26}$ and 88% of 2,3-dimethyl-2,3-diethoxybutane ($C_{10}H_{22}O_2$). These compounds could not be separated by chromatography.

From the lower boiling fractions were isolated: a substance with b.p. 58−60°, n_D^{20} 1.4020, d_4^{20} 0.700, MR_D 28,54; calcd. for C_6H_{10} 28.97 (for diallyl the literature [6] reports b.p. 59.6°, n_D^{20} 1.4044, d_4^{25} 0.6863) and a substance with b.p. 70−73°, n_D^{20} 1.4100, d_4^{20} 0.712, MR_D 29.63; calcd. for C_6H_{12} 29.44 (the literature [7] for 2,3-dimethylbutene-2 reports b.p. 70−71° at 754 mm, n_D^{20} 1.4080, d_0^{20} 0.7007).

An oil and crystals were separated by bromination from the ether distilled off from the reaction products.

The oil had b.p. 87−90° at 35 mm, n_D^{20} 1.5200, d_4^{20} 1.677, MR_D 41,25; calcd. for $C_5H_{10}Br_2$ 40.82. The purity according to Stepanov's method 97.5% reckoned on the dibromo compound. The following data appear in the literature [8] for dibromopentene-1: B.p. 84−85° at 32 mm, d^{15} 1.668.

The crystals separated form the oil had m.p. 167−168° with decomposition (from acetone) and did not give a depression in admixture with the original 2,3-dimethyl-2,3-dibromobutane.

Replacement of allyl chloride by allyl bromide led to formation of the same reaction products but the yield of the fraction with b.p. 145−147° was reduced threefold. The reaction velocity was also lowered appreciably; it only went at a temperature not lower than −10°.

SUMMARY

It was established that of the hydrogen chloride reaction products of the pinacols from methylethyl ketone, methylisobutyl ketone and pinacoline, the most stable is the first member which at 15° in presence of magnesium condenses with one molecule of allyl chloride with cleavage of a molecule of HCl and, without isomerization, forms 3,4-dimethyl-4-allylhexene-2. When the condensation of the above halides is carried out at −20° in presence of magnesium, condensation is effected with two molecules of allyl chloride with formation in 10% yield of 4,5-dimethyl-4,5-diethyloctadiene-1,7. In addition, cleavage of 1 mole. HCl here also leads to C_{11} diolefin, but due to the low velocities of the reaction it undergoes isomerization to 4,5,6-trimethyloctadiene-1,3.

In the condensation of the product of reaction with HBr of the pinacol from acetone (tetramethylethylene dibromide) with allyl chloride in presence of magnesium, the reaction with formation of the hydrocarbon 4,4,5,5-tetramethyloctadiene-1,7 went only to the extent of 12 %. The reaction mainly went anomalously and interaction of the halides with diethyl ether gave the diethyl ether of the pinacol (2,3-dimethyl-2,3-diethoxybutane) and pentene-1.

LITERATURE CITED

[1] E. Marker and T. Oakwood, J. Am. Chem. Soc., 60, 2598 (1938).

[2] G. Calingaert, H. Soroos, V. Hnizda and H. Shapiro, J. Am. Chem. Soc., 66, 1389 (1944).

[3] F. Howard, T. Mears, A. Fookson, P. Pomeranz and D. Brooks, Nat. Bureau of Standard, 38 365 (1947).

[4] A. P. Meshcheryakov, E. I. Erzyutova and A. D. Petrov, Proc. Acad. Sci. USSR, 85, 111 (1952).

[5] A. D. Petrov and M. P. Shebanova, Proc. Acad. Sci. USSR, 84, 72 (1952).

[6] F. Cortese, J. Am. Chem. Soc., 51, 2266 (1929).

[7] N. Kizhner and G. Khonin, J. Russ. Phys. Chem. Soc., 45, 1772 (1913).

[8] H. Dykstra, I. Lewis and C. Boord, J. Am. Chem. Soc., 52, 3400 (1930).

Received December 20, 1954

Moscow Mendeleev Institute of Chemical Technology

CATALYTIC TRANSFORMATION OF ETHYL ALCOHOL UNDER PRESSURE

B. A. Bolotov and L.K. Smirnova

Earlier investigations of the catalytic transformation of ethyl alcohol over copper activated catalysts at the ordinary pressure [1, 2] showed that the direction of these reactions depends upon the temperature. One and the same catalyst at 250–275° directs the reaction toward the formation of ethyl acetate, while in the range of 275–300° the main product of reaction is acetone. Above 300° the formation of higher molecular ketones was observed to predominate.

V. N. Ipatieff and N. A. Klukwin [3], who were the first to investigate the catalytic transformation of ethyl alcohol under pressure, at 530–540°, in presence of alumina, found in the reaction products acetone, isopropyl alcohol, methylethyl ketone, methylethyl carbinol, water and polymethylene hydrocarbons.

In a study of the dehydrogenation of higher alcohols over Cr_2O_3 catalyst at 350–450°, Komarewsky and Coley [4, 5] established the formation of symmetrical ketones; on carrying out the same reaction at higher pressure, Komarewsky and Kritchevsky[6] arrived at the conclusion that aldehydes undergo a series of complex reactions leading to formation of olefinic hydrocarbons containing 2n–1 carbon atoms in the molecule.

The authors of the present paper, as indicated above, established that the direction of the transformation of ethyl alcohol over copper activated catalyst is a function of the temperature. A subsequent study of this process with higher primary alcohols (from propyl to octyl) with the same catalyst demonstrated that they behaved entirely like ethyl alcohol.

At 250–275° these alcohols are transformed into esters in yield of 40–60%; at 325–350° they give symmetrical ketones in yields up to 55% calculated on the original alcohols.

The gaseous products contained more hydrogen and carbon monoxide than the products formed at lower temperatures when the ester-forming condensation takes place.

The changes in composition of the products taking place with rising temperature point to a change in the function of the catalyst. Apparently the ester-forming condensation of aldehyde taking place on the surface of the catalyst at low temperature is replaced at temperatures above 300° by an aldol condensation leading to formation of ketones.

We established that the direction of the reaction of catalytic transformation of primary alcohols is not only a function of the temperature, but depends also upon the pressure during the process. Ethyl alcohol at 350–400° and pressures above 10 atm. gives saturated hydrocarbons corresponding in composition to the ketones obtained in the absence of pressure.

EXPERIMENTAL

Experiments were carried out in a special high-pressure apparatus. With the help of a liquid pump, ethyl alcohol was forced under pressure in the amount of 80–85 g/hour into a vaporizer and from there into the reactor in the form of a steel tube lined with copper and filled with catalyst. The reactor was heated in a block electric furnace. The products of reaction were expanded to atmospheric pressure through a valve and after cooling to –60° they were collected in the form of liquid condensate and gas.

The catalytic transformations of primary alcohols were studied over copper activated catalyst no. 1, investigated previously in the same processes in the absence of pressure [2].

120–130 ml catalyst was charged into the reactor and reduced with hydrogen at 285–300° and atmospheric pressure. After each experiment the condensates were subjected to fractional distillation and were analyzed for content of aldehyde, ester, acid, ketone and saturated hydrocarbons.

The first experiments, conducted with ethyl alcohol at a pressure of 10 atm., had the objective of establishing how the pressure influences the composition of the reaction products in the temperature range of 275–400°. From the data of Table 1 and Fig. 1 we see that the substances obtained under pressure at 275–300° are similar in composition to those previously obtained without pressure. At 300–325° the main products are acetone, methylpropyl ketone and other ketones (methylisobutyl, dipropyl, methylamyl ketone and others). At 325° and higher under pressure, new compounds are formed – saturated hydrocarbons which are absent when the process is conducted without pressure; their yield increases with rising temperature. At the same time the carbon dioxide content of the gaseous products increases and the water content of the condensates increases. At 350–400° the condensates consist solely of saturated hydrocarbons and water. Evidently, rise of pressure at these temperatures promotes a fresh hydrogenation reaction resulting in formation of saturated hydrocarbons. In the "oily" layer of the condensates were detected pentane, hexane, and heptane whose contents of carbon atoms in the chains correspond to the ketones obtained in the experiments without pressure; higher hydrocarbons are also present – octanes, nonanes, decanes, etc., the content of which increases with rising temperature.

In order to establish the relation between pressure and composition of the products of transformation of ethyl alcohol obtained at various temperatures, experiments were run at 300° (when the main products of reaction were ketones) and at 350° (the optimum for the yield of saturated hydrocarbons). In Table 2 are presented the results of experiments at 300° and pressures of 1 to 120 atm. The condensates under these conditions were homogeneous and did not contain water.

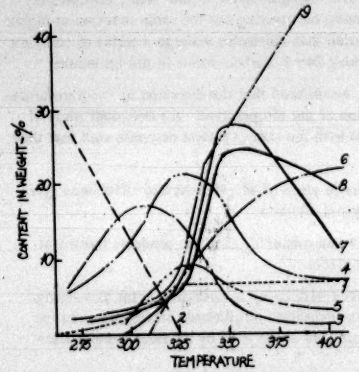


Fig. 1. Change of composition of products of reaction of ethyl alcohol with respect to temperature at a pressure of 10 atm.

1) acetaldehyde; 2) ethyl acetate; 3) acetone; 4) methylpropyl ketone; 5) dipropyl ketone; 6) water; 7) pentane and hexane; 8) heptane; 9) higher hydrocarbons C >7.

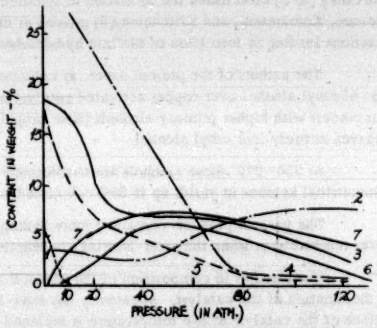


Fig. 2. Composition of products of reaction of ethyl alcohol at 300° with respect to pressure.

1) acetaldehyde; 2) ethyl acetate; 3) acetone; 4) methylpropyl ketone; 5) higher ketones C >5; 6) saturated hydrocarbons C_5–C_7; 7) hydrocarbons C >7.

Rise of pressure to 20 atm. was scarcely reflected in the composition of the condensates, whereas a rise to 40 atm. and higher caused a sharp drop in the yield of ketones. At 120 atm. their yield was not more than 6–8%, since at high pressures and a temperature of 300° the rate of dehydrogenation of alcohol to aldehyde falls sharply, and the amount of unreacted alcohol in the condensate rises from 10 to 62%. Under these conditions the content of saturated hydrocarbons in the condensate does not exceed 10–12%.

From the experiments at 350° and pressures of 5 to 160 atm. presented in Table 3 and Fig. 3, we see that the specified conditions are the optimum for preparation of saturated hydrocarbons. Their content in the "oily" layer of condensate reaches 95%. With rise of pressure from 5 to 160 atm. the pentane content increases

TABLE 1

Catalytic conversion of ethyl alcohol under a pressure of 10 atm.

Temperature	Yield of condensate (weight-%)	Content in condensate (weight-%) of: acetaldehyde	pentane	acetone	hexanes	ethyl acetate	ethyl alcohol	heptane	methyl-propyl ketone	octanes	methyl-isobutyl ketone	nonanes	dipropyl ketone	higher ketones	saturated hydrocarbons $>C_9$	water
275°	75.2	0.5	0.0	8.4	0.0	25.0	57.5	2.4	6.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
300	75.0	1.0	0.0	16.3	0.5	11.6	34.9	1.5	11.7	2.1	1.3	0.9	1.9	0.0	0.0	0.0
325	57.0	6.4	0.0	14.9	5.8	0.0	12.0	5.4	20.9	3.5	4.1	4.5	9.0	0.0	0.0	7.4
350	57.7	5.9	14.5	3.3	13.9	0.0	0.0	24.2	3.8	8.6	0.4	11.3	1.5	1.2	6.8	15.2
400	66.5	6.0	8.6	1.2	3.8	0.0	0.0	19.8	7.0	11.7	1.7	8.7	3.4	2.6	27.0	21.7

TABLE 2

Catalytic conversion of ethyl alcohol with respect to pressure at 300°

Pressure (atm.)	Yield of condensate (weight-%)	Content in condensate (weight-%) of: acetaldehyde	saturated hydrocarbons C_3-C_7	acetone	ethyl acetate	methyl-propyl ketone	methyliso-butyl ketone	dipropyl ketone	saturated hydrocarbons C_8-C_9	saturated hydrocarbons $>C_9$
Atmospheric	64.2	6.6	0.0	18.2	2.8	33.0	3.0	13.6	0.0	0.0
5	71.0	1.7	0.0	18.0	3.5	27.1	4.4	7.0	1.2	0.2
10	57.7	0.0	0.8	17.7	0.7	32.7	1.6	14.3	3.3	0.6
20	71.0	0.0	0.8	8.6	3.2	24.0	0.7	6.4	3.0	2.2
40	55.5	0.2	6.0	6.8	2.3	15.0	1.6	3.2	3.7	3.0
80	74.5	0.0	4.4	6.6	6.7	1.0	0.2	1.4	3.1	0.0
120	79.5	0.0	1.1	2.5	7.1	0.6	0.1	1.6	4.4	0.0

TABLE 3

Effect of pressure on catalytic conversion of ethyl alcohol

Pressure (atm.)	Yield of condensate (weight-%)	Content in condensate (weight-%) of													
		acetaldehyde	pentane	acetone	hexanes	ethyl acetate	heptane	methylpropyl ketone	octanes	methylisobutyl ketone	nonanes	dipropyl ketone	higher ketones	saturated hydrocarbons $>C_9$	water
5	61.2	5.7	6.2	5.2	5.9	0.7	7.0	21.1	2.6	4.0	4.5	7.3	4.6	10.2	16.9
10	57.7	5.9	14.5	3.3	13.9	0.0	24.2	3.8	8.6	0.4	11.3	1.5	1.2	6.8	15.2
40	56.1	0.9	46.6	0.6	6.9	0.0	25.0	1.8	6.6	0.1	5.4	1.1	0.8	5.4	18.3
80	53.3	0.3	61.2	2.8	5.9	0.0	18.7	0.7	3.9	0.1	2.6	0.1	0.0	1.8	23.4
156	57.8	1.0	73.2	0.5	4.0	3.6	10.0	0.2	0.5	0.3	3.7	0.0	0.0	0.0	29.9

TABLE 4

Properties of hydrocarbon fractions

Hydrocarbon fractions	Pressure (atm.)					Literature data [7]	
	10	40		80	156		
	n_D^{20}	n_D^{20}	molecular weight	n_D^{20}	n_D^{20}	n_D^{20}	molecular weight
n-Pentane	–	1.3577	73.3	1.3578	1.3583	1.3577	72
Hexane	–	1.3765	87.2	1.3760	1.3742	1.3757	86
n-Heptane	1.3883	1.3880	101.0	1.3882	1.3882	1.3877	100
Octane (110–118°)	1.3043	1.3962	113.8	1.3960	1.3918	1.3976	114
n-Nonane	1.4043	1.4060	126.0	1.4058	1.4058	1.4056	128
Decane (162–165°)	–	1.4118	145.7	1.4133	–	1.4123	142

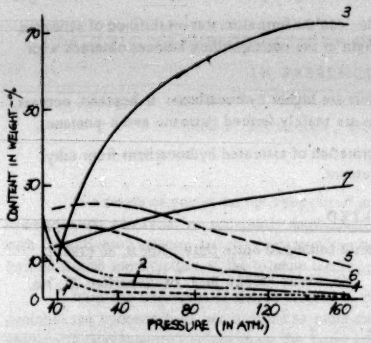


Fig. 3. Composition of products of reaction of ethyl alcohol at 350° in dependence on the pressure.

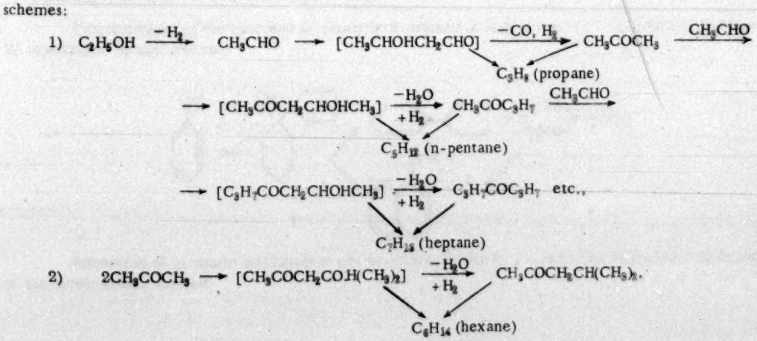
1) acetaldehyde; 2) ketones (total); 3) pentane; 4) hexane; 5) heptane; 6) hydrocarbons C 7; 7) water.

considerably: at 5 atm. the yield is 6%, at 156 atm. it is 73%, and the yield of higher hydrocarbons falls at the same time. The maximum amount of higher hydrocarbons is obtained at 10 atm.: the presence of hexanes, heptane, octanes, nonane and other high-molecular hydrocarbons was established. The predominating hydrocarbon is n-heptane, the yield of which reaches 25% at 10–20 atm. Rise of pressure lowers the formation of heptane and other higher hydrocarbons and correspondingly increases the yield of petane.

The presence of pentane and propane in the gas may be explained by the possibility of hydrogenation of the initially formed acetone and methylpropyl ketone, the velocity of this reaction at 350° and pressures above 20 atm. considerably exceeding the velocity of condensation of acetone and methylpropyl ketone to higher ketones. Condensation of acetone with acetaldehyde is interrupted at the stage of formation of methylpropyl ketone, which is nearly quantitatively reduced to n-pentane. The yield of n-pentane rises from 6 to 73%. The presence in the condensate of up to 30% water supports this scheme.

Very small amounts of ester were detected in the condensate, evidently because aldehyde formed during dehydrogenation of the alcohol is transformed according to the aldol mechanism into acetone, methylpropyl ketone and other ketones, which under pressure are transformed into saturated hydrocarbons. The carbon monoxide formed during the reaction is converted, in presence of water, nearly completely into carbon dioxide and hydrogen.

Formation of ketones and saturated hydrocarbons from ethyl alcohol can be represented in the following schemes:


1) $C_2H_5OH \xrightarrow{-H_2} CH_3CHO \longrightarrow [CH_3CHOHCH_2CHO] \xrightarrow{-CO,\ H_2} CH_3COCH_3 \xrightarrow{CH_3CHO}$
C_3H_8 (propane)
$\longrightarrow [CH_3COCH_2CHOHCH_3] \xrightarrow[+H_2]{-H_2O} CH_3COC_3H_7 \xrightarrow{CH_3CHO}$
C_5H_{12} (n-pentane)
$\longrightarrow [C_3H_7COCH_2CHOHCH_3] \xrightarrow[+H_2]{-H_2O} C_3H_7COC_3H_7$ etc.,
C_7H_{16} (heptane)
2) $2CH_3COCH_3 \longrightarrow [CH_3COCH_2COH(CH_3)_2] \xrightarrow[+H_2]{-H_2O} CH_3COCH_2CH(CH_3)_2$.
C_6H_{14} (hexane)

In Table 4 are presented the experimentally determined coefficients of refraction and the molecular weights of the hydrocarbons obtained under pressures of 10 to 156 atm. From the data we can conclude that the hydrocarbons isolated from the fractions at temperatures of 31–36° correspond to n-pentane, the 90–98° fractions to n-heptane, and the 118–120° fractions to n-nonane. The other fractions are evidently mixtures of hydrocarbons of normal and iso structures.

SUMMARY

1. Ketones (acetone, methylpropyl ketone, methylisobutyl ketone, dipropyl ketone and higher ketones) are formed from ethyl alcohol at 300–350° and pressures not exceeding 5 atm. over copper activated catalyst.

2. At pressures of 20–150 atm. and temperatures of 350–400°the formation was established of saturated hydrocarbons with the same number of carbon atoms in the chain as the corresponding ketones obtained without pressure.

3. At pressures of 10–20 atm. the main reaction products are higher hydrocarbons: n-heptane, octanes, n-nonane, etc.; at pressures above 20 atm. lower hydrocarbons are mainly formed (propane and n-pentane).

4. The experimental data justify the conclusion that formation of saturated hydrocarbons from ethyl alcohol is preceded by the stages of formation of aldols and ketones.

LITERATURE CITED

[1] B. N. Dolgov, B. A. Bolotov and K. P. Katkova, Vestnik Leningrad State Univ., No. 6, 35 (1950).

[2] B. A. Bolotov and B. N. Dolgov, Author's Report No. 92622 (1950); Bull. of Inventions XI, No. 11, 12 (1951).

[3] V. N. Ipatieff and N. A. Klukwin, Ber., 58, 4 (1925).

[4] V. I. Komarewsky and I. R. Coley, J. Am. Chem. Soc., 63, 700 3269 (1941).

[5] J. R. Coley and K. I. Komarewsky J. Am. Chem. Soc., 68, 716 (1946).

[6] V. I. Komarewsky and T. H. Kritchevsky, J. Am. Chem. Soc., 65, 547 (1943).

[7] E. Huntress and S. Mulliken, Identif. of Pure Organic Compounds (1946).

Received July 17, 1954

Leningrad State University

CATALYTIC TRANSFORMATIONS OF 1-METHYL-1-CYCLOPENTYL-CYCLOHEXANE IN PRESENCE OF PLATINIZED CARBON

S. I. Khromov, O. V. Bragin and E. S. Balenkova

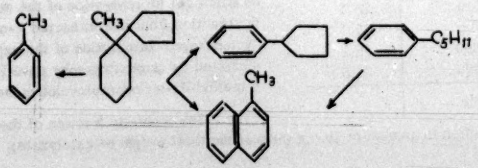
In a series of papers on the behavior of some gem-methylalkylcyclohexanes under conditions of dehydrogenation catalysis, we previously established that gem-methylalkylcyclohexanes undergo dehydrogenation with formation of toluene and the corresponding monoalkylbenzene. At the same time o- and m-xylenes were formed due to methylation of the toluene resulting from the catalysis [1].

With the objective of further clarifying the characteristic features of the behavior of gem-substituted cyclohexane hydrocarbons, we decided to study the behavior under conditions of dehydrogenating catalysis of gem-methylcyclopentylcyclohexane; the latter is a disubstituted hexamethylene hydrocarbon in which one of the geminal radicals is the pentamethylene radical. For this purpose the synthesized 1-methyl-1-cyclopentylcyclohexane was brought into contact at 320° with 10% platinized carbon. The catalyzate mixture was subjected to chromatographic adsorption on silica gel wherby unreacted original hydrocarbon was separated from the aromatic hydrocarbons formed; the latter were fractionally distilled in a column. The compositions of the individual fractions were established by oxidation with aqueous permanganate solution.

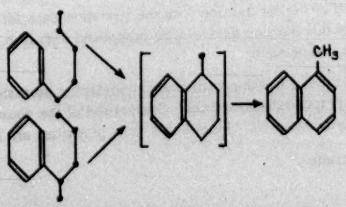
On the basis of the physical constants of the individual fractions of the aromatic portion of the catalyzate and of the results of their chemical analysis, some conclusions were drawn about the composition of the catalyzate and about the directions of the transformations of 1-methyl-1-cyclopentylcyclohexane under our selected conditions.

The composition of the mixture of aromatics obtained by catalytic transformation of 1-methyl-1-cyclopentylcyclohexane over platinized carbon is roughly as follows: toluene ~ 6%, amylbenzene ~9%, phenylcyclopentane ~ 68%, α-methylnaphthalene ~ 17%.

The directions of the reactions of catalytic transformations of 1-methyl-1-cyclopentylcyclohexane can be represented by the scheme:



Formation of α-methylnaphthalene can be accounted for by the following secondary transformations of the amylbenzene formed:



Under experimental conditions similar to ours, S. R. Sergienko also reported dehydrogenation of isoamylbenzene to β-methylnaphthalene [2].

The above reaction scheme and the results of catalytic transformation of 1-methyl-1-cyclopentylcyclohexane point to the occurrence of several reactions under our selected experimental conditions: Firstly, the original hydrocarbon is dehydrogenated and hydrogen atoms are split off not only in the hexamethylene ring but also from one of the geminal alkyl groups. The methyl groups are preferentially cleaved and this reaction gives phenylcyclopentane. Secondly the five-membered ring of phenylcyclopentane undergoes hydrogenolysis to give a mixture of isomeric amylbenzenes. Finally, under the conditions of dehydroganation catalysis, the amylbenzenes undergo dehydrocyclization to form α-methylnaphthalene.

EXPERIMENTAL

Synthesis of 1-methyl-1-cyclopentylcyclohexane

To an ethereal solution of magnesium cyclopentyl chloride was added mercuric chloride, and an ethereal solution of 1-chloro-1-methylcyclohexane was slowly introduced. The reaction mixture was heated at the boiling point of ether for about 20 hours; the main bulk of ether was then distilled off and dry toluene was run into the flask; the mixture was then heated 15 hours at the boiling point of toluene. The reaction mixture was then decomposed with cold, acidified water; after driving off the ether and toluene, the residue was boiled with metallic sodium before fractioning in vacuum.

35.5 g (6.5%) 1-methyl-1-cyclopentylcyclohexane was obtained.

B.p. 95–96° (12 mm), n_D^{20} 1.4830, d_4^{20} 0.8852. MR_D 53.53; Calcd. 53.22.

Found %: C 86.86, 86.71; H 13.20, 13.16. $C_{12}H_{22}$. Calcd. %: C 86.74; H 13.26.

1-Methyl-1-cyclopentylcyclohexane has not been described in the literature.

Catalytic transformations of 1-methyl-1-cyclopentylcyclohexane

35.5 g of the hydrocarbon was passed over 10% platinized carbon at 320° (without a carrier gas) at a space velocity of 0.2. Results of the experiments are detailed in the table.

TABLE

Pass	n_D^{20}	Amount of gas evolved (in ml)	Weight of catalyzate (in g)
1	1.4980	5010	33.4
2	1.5013	1700	32.7
3	1.5033	800	32.1
4	1.5060	790	31.6
	Total	8300	

The gaseous products of reaction were analyzed in a VTI* apparatus. Results of gas anaylsis: H_2 94.8%, CH_4 5.0%.

The catalyzate, a colorless liquid weighing 31.6 g, was subjected to chromatographic adsorption on silica gel for separation of the aromatics formed in the reaction from the unreacted 1-methyl-1-cyclopentylcyclohexane. Distillation of the naphthenic fraction separated by chromatography gave 20.7 g of the original 1-methyl-1-cyclopentylcyclohexane.

The aromatic fraction of the catalyzate, obtained by chromatographic adsorption in amount of 10.5 g (38% of the total weight of catalyzate), was fractionated in a column (at 740 mm).

Fractions obtained: 1st 109–114°, n_D^{20} 1.4970, d_4^{20} 0.8663; 4.7%; 2nd 114–185°, n_D^{20} 1.4903, 1.9%; 3rd 185–203°, n_D^{20} 1.4881, d_4^{20} 0.8605, 7.2%; 4th 203–214°, n_D^{20} 1.4833, 1.9%; 5th 214–217°, n_D^{20} 1.5312, d_4^{20} 0.9515, 59.0%; 6th 217–235°, n_D^{20} 1.5395, 2.8%; 7th 235–242°, n_D^{20} 1.6160, d_4^{20} 0.9993, 16.7%.

Comparison of the constants of the 1st fraction with the literature data for toluene shows that it consists mainly of toluene. Nitration of this fraction gave a nitro compound with m.p. 69°. A mixed melting test with 2,4-dinitrotoluene did not give a depression.

3rd fraction. Oxidation of the 3rd fraction with aqueous potassium permanganate gave benzoic acid, thus confirming that it contained only monoalkylbenzenes. Comparison of the constants of this fraction with the constants of some isomers of amylbenzene [3, 4] shows that their properties are identical.

* All – Union Heat Engineering Institute.

5th fraction. Oxidation gave only benzoic acid. The physical properties of the 5th fraction are very similar to those of phenylcyclopentane for which N. D. Zelinsky and I. N. Titz [5] report: b.p. 215–217° (760 mm), n_D^{20} 1.5305, d_4^{20} 0.9503.

7th fraction. Treatment with picric acid brings down a yellow crystalline picrate with m.p. 140°. Judging by the physical properties and the ability to form a picrate, this fraction consists mainly of α-methylnaphthalene.

Literature data for α-methylnaphthalene: picrate, m.p. 141–142° [7]; b.p. 121–123° (20 mm), n_D^{20} 1.6173, d_4^{20} 1.0120 [6].

SUMMARY

A study was made of the catalytic transformations of 1-methyl-1-cyclopentylcyclohexane in presence of platinized carbon at 320°; it was established that the reactions proceed with formation of phenylcyclopentane, toluene, isomeric amylbenzenes and α-methylnaphthalene.

LITERATURE CITED

[1] B. A. Kazansky and A. L. Liberman, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1947, 265; S. I. Khromov, E. S. Balenkova and B. A. Kazansky, Proc. Acad. Sci. USSR, 96, 95, 295 (1954); S. I. Khromov, E. S. Balenkova, P. A. Akishin and B. A. Kazansky, Proc. Acad. Sci. USSR, 97, 103 (1954).

[2] S. P. Sergienko, Proc. Acad. Sci. USSR, 27, 960 (1940).

[3] N. Toussaint and G. Hennion, J. Am. Chem. Soc., 62, 1145 (1940).

[4] V. Ipatieff and L. Schmerling, J. Am. Chem. Soc., 60, 1476 (1938).

[5] N. D. Zelinsky and I. N. Titz, Ber., 58, 2755 (1925).

[6] E. Evans, J. Inst. Petroleum Technol., 24, 537 (1938).

[7] R. Meyer and H. Fricke, Ber., 47, 2770 (1914).

Received October 30, 1954

Moscow State University

ISOMERIZATION OF UNSATURATED HYDROCARBONS BY THE ACTION OF CALCIUM AMIDE

I. V. Gostunskaya and B. A. Kazansky

B. A. Kazansky and co-workers [1–3], in a study of the reduction of aromatic and diene hydrocarbons with the help of calcium ammine—which breaks down according to the equation $Ca(NH_3)_6 \rightarrow Ca(NH_2)_2 + 4NH_3 + H_2$[4, 5], – observed that diene hydrocarbons not possessing a conjugated system of double bonds give the same reaction products as are obtained by reduction of their isomeric conjugated dienes. The authors advanced the hypothesis that isomerization [3] of the hydrocarbon preceds reduction and they confirmed this by the isolation, for example in the reduction of diisobutylene (2,5-dimethylhexadiene-1,5), of diisocrotyl (2,5-dimethylhexandiene-2,4) as intermediate product, the latter possessing a conjugated system of double bonds [3].

The present work was undertaken for the purpose of further study of this phenomenon. We showed that the isomerizing agent is not calcium ammine itself but the product of its breakdown – calcium amide; we were the first to observe the isomerizing action of calcium amide on olefinic hydrocarbons; cases are known, however, of the isomerization of multiple bonds in hydrocarbons of various classes by the action of sodium and potassium amides. For example, 2-heptyne and 3-heptyne isomerize to 1-heptyne in good yield in presence of sodium amide at a temperature of 160–170° [6].

With excess sodium amide at about 140°, hexadiene-1,2 and 5-methylhexadiene-1,2 form the sodium derivatives of alkynes-1 [7]. 4-Cyclohexylbutyne-2,5-cyclohexylpentyne-2 and 6-cyclohexylhexyne-2, in presence of sodium amide at 160°, likewise isomerize to the corresponding cyclohexylalkynes-1-[8].

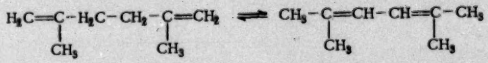
In all the cases cited above, isomerization with sodium amide proceeds at elevated temperatures; in liquid ammonia solution the isomerization also goes at low temperatures. Thus Hückel and Bretschneider [9] observed the isomerizing action of a solution of sodium amide in liquid ammonia on 1,4-dihydronaphthalene which at –70° was wholly converted into 3,4-dihydronaphthalene.

The isomerizing action of potassium amide at low temperatures was observed by Shatenshtein and co-workers [10] when studying the lability of hydrogen in aliphatic hydrocarbons in deuterium exchange reactions when acting on them with deuteroammonia in presence of potassium amide as a catalyst for the exchange reaction. Under these conditions α-olefins (pentene-1, hexene-1 and octene-1) isomerized to olefins with double bonds more distant from the end of the hydrocarbon chain. Under these conditions diallyl (1,5-hexadiene) isomerized to dipropenyl 2,4-hexadiene which polymerized in presence of potassium amide.

We studied the isomerizing action of calcium amide on mono- and diolefins at their boiling points. Isomerization of monoolefins resulted in shifting of the double bond to the center of the molecule; the extent of this transformation depends upon the structure of the original hydrocarbon: 2-methylbutene-1 and 3-methylbutene-1 were nearly completely transfromed into 2-methylbutene-2; 2-methylbutene-2 remained unchanged under the conditions employed; 2-methylhexene-2 only partly isomerized to hydrocarbons whose structure was not established.

The diolefinic hydrocarbons hexadiene-1,5, 2-methylhexadiene-1,5 and 2,5-dimethylhexadiene-1,5, with double bonds far apart, easily isomerized to diolefins containing a system of conjugated double bonds to the extent of about 90%. This reaction can serve as a convenient preparative method for conjugated dienes, starting from dienes whose double bonds are far apart.

Investigation of the optimum conditions of isomerization showed that this reaction goes with appreciable velocity in the absence of solvents only when heated, although there is no doubt that under the conditions of reduction of hydrocarbons with well-spaced double bonds such as diisobutylene [3, 11], i.e. at 0–10° or room temperature, the isomerization (which precedes reduction) goes without heating. This phenomenon can evidently be explained by a shift of the equilibrium to the right:



due to the removal of diisocrotyl from the sphere of the reaction by reduction, or to the presence of hydrogen which facilitates the isomerization.

In the experiments carried out in this work, isomerization was effected by gentle boiling of the hydrocarbon mixture, but the possibility of carrying out this reaction at lower temperatures is not excluded.

It was ascertained that about 0.35 mole calcium amide per mole of diene was adequate for isomerization of diene hydrocarbons.

EXPERIMENTAL

Preparation of calcium amide. A weighed amount of metallic calcium was treated with dry ammonia under cooling at −5 to −10° for 4 hours. As preliminary experiments with suspended products of addition of calcium to ammonia showed, under such conditions rather more than 5 molecules of ammonia combine, after which there is no further increase in weight. The reason is that partial decomposition of the calcium ammine proceeds side by side with the addition of ammonia (see equation above).

The prepared calcium ammine was left for several days in a flask from which external moisture was excluded by a tube filled with solid potassium hydroxide. After three days the calcium ammine was transformed into calcium amide in 99% yield as evident from the data of Table 1.

TABLE 1

Weight of Ca (in g)	Weight of $Ca(NH_3)_6$ (in g)	Weight of products of decomposition of calcium ammine (in g)					Calculated amount of amide (in g)	Yield of amide (in %)
		after 1 day	after 2 days	after 3 days	after 4 days	after 18 days		
5.0	15.9	10.9	9.9	8.9	8.9	8.9	9.0	99
5.0	15.7	11.2	10.0	9.0	8.9	8.9	9.0	99

Procedure for isomerization experiments. The reaction was carried out either in a catalytic tube (with or without heating) or in a round-bottom flask with a reflux condenser. In the latter case, after heating of the reaction mixture for 1−2 hours, the reaction products were distilled from the reaction flask. The composition of the products of isomerization was investigated by two methods: when large amounts of hydrocarbons were subjected to isomerization, the mixture obtained was fractionated in a column and the individual hydrocarbons were collected and their specific gravity and refractive index were determined. When not more than 5 to 10 ml of hydrocarbon was taken in an experiment, the extent of their polymerization was evaluated from the change in refractive index of the mixture.

Isomerization of mono-olefinic hydrocarbons. a) Isomerization of 3-methylbutene-1, 2-methylbutene-2 and 2-methylbutene-1. The first two amylenes were obtained by dehydration of isoamyl alcohol over alumina; 2-methylbutene-1 was separated from the products of incomplete hydrogenation of isoprene. After distillation in a column of 70 theoretical plates, the olefins possessed the properties shown in Table 2. The same table contains literature data for isopentenes.

TABLE 2

Hydrocarbon	Constants of synthesized hydrocarbons			Literature data [12]		
	Boiling point at 760 mm	n_D^{20}	d_4^{20}	Boiling point at 760 mm	n_D^{20}	d_4^{20}
5 3-Methylbutene-1	20.2°	1.3648	0.6296	20.06°	1.3643	0.6272
6 2-Methylbutene-1	31.2	1.3784	0.6500	31.16	1.3778	0.6504
7 2-Methylbutene-2	38.5	1.3881	0.6613	38.53	1.3874	0.6623

Isomerization was performed with a calcium amide/hydrocarbon molar ratio of 2:1 with gentle boiling of the olefins for 2 hours.

The catalyzates had the following properties:	n_D^{20}	d_4^{20}
Product of isomerization of 3-methylbutene-1	1.3810	0.6523
" " 2-methylbutene-1	1.3870	0.6597
" " 2-methylbutene-2	1.3878	0.6610

2-Methylbutene-2 was substantially unchanged under the experimental conditions, while 3-methylbutene-1 and 2-methylbutene-1 were nearly entirely transformed into 2-methylbutene-2.

Isomerization of 2-methylhexene-2. The starting 2-methylhexene-2 was obtained by partical reduction of 2-methylhexadiene-2,4 with calcium amide. After distillation in a column of 70 theoretical plates the hydrocarbon had the constants:

B.p. 94.6° at 760 mm, n_D^{20} 1.4100, d_4^{20} 0.7080. Literature data [13]: b.p. 95.0 (760 mm), n_D^{20} 1.4075, d_4^{20} 0.7089.

For the isomerization 14 ml (9.8 g) hydrocarbon and 29 g calcium amide were taken. After heating at the boil for 2 hours, 13 ml catalyzate was distilled with n_D^{20} 1.4070 and d_4^{20} 0.7049. Fractionation in a column gave two fractions: 1st 5 ml with b.p. 86.5–94.5°, n_D^{20} 1.4050, d_4^{20} 0.6999, and 2nd 7 ml with b.p. 94.5°, n_D^{20} 1.4098, d_4^{20} 0.7082.

The second fraction contained unchanged original hydrocarbon, while the 1st fraction was a mixture of original olefin and prducts of isomerization with lower constants than the original hydrocarbon; the content of the latter, judging by the constants of the fraction, was low.

Isomerization of diolefinic hydrocarbons. The starting hexadiene-1,5, 2-methylhexadiene-1,5 and 2,5-dimethylhexadiene-1,5 were obtained by reaction between allyl chloride and methallyl chloride in presence of magnesium in ether solution. The constants of the dienes obtained and the literature data for them are set forth in Table 3.

a) Isomerization of hexadiene-1,5. 26.7 g calcium amide and 33 ml (23 g) diene were taken. After refluxing for 2 hours in a flask, 30 ml catalyzate with n_D^{20} 1.4520 was distilled off. Fractionation of 25 ml catalyzate in a column of 70 theoretical plates gave two fractions:

1st 3.8 ml, b.p. 68.5° (760 mm), n_D^{20} 1.4340; 2nd 18.0 ml, b.p. 82.0° (760 mm), n_D^{20} 1.4535; d_4^{20} 0.7177; residue 2.5 ml, n_D^{20} 1.44540.

Losses in the column packing amounted to 0.7 ml.

The 2nd fraction, the still residue and the losses in the column packing amounted to 86% of the volume of catalyzate; they consisted of dipropenyl, a product of isomerization of hexadiene-1,5 whose constants are given in Table 4.

TABLE 3

Hydrocarbon	Constants of synthesized hydrocarbons			Literature data [14]		
	Boiling point at 760 mm	n_D^{20}	d_4^{20}	Boiling point at 760 mm	n_D^{20}	d_4^{20}
5 Hexadiene-1,5 (diallyl)	59.2°	1.4042	0.6935	59.4°	1.4040	0.6916
6 2-Merhylhexadiene-1,5	89.1	1.4195	0.7202	88.1	1.4184	0.7198
7 2,5-Dimethylhexadiene-1,5	114.4	1.4302	0.7447	114.3	1.4293	0.7423

The 1st fraction consists of a mixture of the original diallyl and dipropenyl.

b) Isomerization of 2-methylhexadiene-1,5. 35.5 g calcium amide and 90 g (125 ml) hydrocarbon were taken. Heating of the mixture for 2 hours at the boil gave 120 ml catalyzate with n_D^{20} 1.4665.

Fractional distillation of the catalyzate in a column of 70 theoretical plates gave the following fractions:

1st 14.0 ml, b.p. 92–111.6°, n_D^{20} 1.4525; 2nd 100.0 ml, b.p. 111.6°, n_D^{20} 1.4684, d_4^{20} 0.7448; residue 4.0 ml, n_D^{20} 1.4685; losses 2.0 ml.

The 2nd fraction, the still residue and losses in the column packing (about 1 ml), consisting of 2-methylhexadiene-2,4 (Table 4), made up 87% of the volume of catalyzate. The 1st fraction likewise contains mainly the product of isomerization with a small admixture of original diene.

c) Isomerization of 2,5-dimethylhexadiene-1,5. 26 g calcium amide and 22.8 g (30 ml) diisobutylene were taken for isomerization. Refluxing for 1½ hours in a round-bottomed flask gave 27 ml catalyzate with n_D^{20} 1.4715. Fractional distillation in a column of 70 theoretical plates gave the following fractions:

1st 2.2 ml, b.p. 100–114°, n_D^{20} 1.4255; 2nd 3.5 ml, b.p. 114–134.7°, n_D^{20} 1.4430; 3rd 17.0 ml, b.p. 134.7°, n_D^{20} 1.4782, d_4^{20} 0.7642; residue 3.0 ml, n_D^{20} 1.4798; losses in column 1.3 ml.

The 3rd fraction, the still residue and the losses in the column packing totalled 21 ml, representing 80% of the volume of catalyzate taken for fractional distillation; it was diisocrotyl (Table 4). The 2nd fraction contained a mixture of the original diisobutylene with diisocrotyl. The first fraction, boiling below the original diene, contained reaction products that were not identified.

Determination of optimum conditions of isomerization. The starting hydrocarbon was diisobutylene with the constants detailed in Table 3.

a) Influence of temperature. Experiments were carried out in a flask at the boiling point of the hydrocarbon mixture and in a catalytic tube with and without heating. Results are presented in Table 5.

TABLE 4

Hydrocarbon	Boiling point	n_D^{20}	d_4^{20}
3 Hexadiene-2,4 (dipropenyl) [15]	82.0°	1.4535	0.7142
4 2-Methylhexadiene-2,4 [16]	111.5	1.4680	0.7449
5 2,5-Dimethylhexadiene-2,4 [16]	134.5	1.4781	0.7615

TABLE 5

Diene taken (in ml)	Temperature of experiment	Catalyzate obtained (in ml)	n_D^{20} of catalyzate	Percent isomerization	Apparatus
5.0	19°	3.5	1.4304	0	Catalytic tube
5.0	18	3.5	1.4300	0	
3.5	150	2.0	1.4676	76.2	
5.0	150	3.6	1.4698	82.0	Flask

At room temperature diisobutylene does not isomerize.

b) Influence of duration of contact band of the amount of amide. Experiments were conducted in a flask. Results are presented in Table 6.

Comparison of the results of the experiments (Table 6) shows that under otherwise identical conditions a decrease in the duration of contact from 2 hours to 1 hour favourably influences the yield of diisocrotyl, evidently due to suppression to some extent of any side reactions. The comparison also shows that reduction in the amount of amide to 0.33 mole per mole hydrocarbon does not reduce the yield of diisocrotyl.

TABLE 6

Amount of diisobutylene (in ml)	Amount of diisobutylene (in g)	Amount of amide (in g)	Ratio of $Ca(NH_3)_6$: C_8H_{14} (in moles)	Duration of contact (hours)	Amount of catalyzate (in ml)	n_D^{20}	Percent of isomerization
15.0	11.4	26.0	3.6	2	13.0	1.4685	80.0
15.0	11.4	26.0	3.6	1	13.5	1.4745	91.0
11.4	8.5	1.7	0.33	1	10.0	1.4732	89.0
11.4	8.5	1.7	0.33	1	10.0	1.4741	90.0

SUMMARY

1. A study was made of the isomerizing action of calcium amide, obtained by the spontaneous breakdown of calcium ammine, on mono- and diolefinic hydrocarbons at the boiling points of the hydrocarbons.

The main direction of isomerization of the investigated monoolefins was translocation of the double bond to the center of the molecule, the extent of this conversion depending upon the structure of the starting molecule.

3. Diolefinic hydrocarbons whose double bonds are far apart are easily isomerized by calcium amide to form dienes with conjugated double bonds; this reaction can serve for the preparation of conjugated dienes.

LITERATURE CITED

[1] B. A. Kazansky and N. V. Smirnova, Bull. Acad. Sci. USSR, Div. Math. and Nat. Sci., 1937, 547.

[2] B. A. Kazansky and N. F. Glushnev, J. Gen. Chem., 8, 642 (1937).

[3] B. A. Kazansky and N. F. Glushnev, Bull. Acad. Sci. USSR, Div. Math. and Nat. Sci., 1938, 1065.

[4] W. Biltz and G. Huttig, Z. allg. anorg. Chem., 114, 241 (1920).

[5] E. Botolfsen, Ann. Chim., (9) 18, 5 (1922); Bull. Soc. Chim., (4) 31, 561 (1922).

[6] H. H. Guest, J. Am. Chem. Soc., 50, 1744 (1928).

[7] M. Bouis, Ann. Chim., (10) 9, 403 (1928).

[8] M. Bourguel, Ann. Chim., 3, 325 (1925); Comptes rend., 179, 686 (1924).

[9] W. Hückel and H. Bretschneider, Ann., 540, 172 (1939).

[10] A. I. Shatenshtein, L. N. Vasilyeva, N. M. Dykhno and E. A. Izrailevich, Proc. Acad. Sci. USSR, 85, 381 (1952).

[11] B. A. Kazandky and I. V. Gostunskaya, Proc. Acad. Sci. USSR, 76, 407 (1951).

[12] Selected Values of Properties of Hydrocarbons. Washington (1947).

[13] F. J. Soday and C. E. Boord, J. Am. Chem. Soc., 55, 3293 (1933).

[14] A. Henne, H. Chanan and A. Turk, J. Am. Chem. Soc., 63, 3474 (1941).

[15] A. Henne and H. Chanan, J. Am. Chem. Soc., 66, 395 (1944).

[16] A. Henne and A. Turk, J. Am. Chem. Soc., 64, 280 (1942).

Received October 23, 1954

Moscow State University

SYNTHESIS OF FARNESOL AND FARNESAL

I. K. Sarycheva, N. G. Morozova, V. A. Abramovich, S. A. Brietburt, L. F. Sergienko and N. A. Preobrazhensky

Farnesol (2,6,10-trimethyl-dodecatrien-2, 6,10-ol-12) is the odorous principle of the flowers of lily-of-the-valley, lime, false acacia and vegetable musk and of several other essential oils.

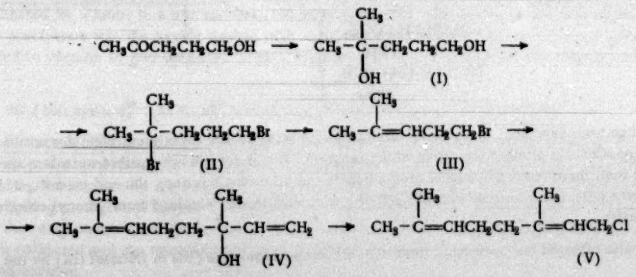
In the first attempt to prepare farnesol [1] the starting substance was natural geraniol, and farnesol was formed by successive steps of condensation, hydrolysis, dehydration and reduction (sodium in alcohol). Another synthesis starts from geraniol and the intermediates are geranyl chloride, α,β-dihydropseudoionone and nerolidol [2].

The main defect of these semi-syntheses is the variable course of the reactions of hydrogenation and dehydration, resulting in the formation of a complex mixture of substances with a very small content of farnesol.

In the present paper we describe for the first time a complete synthesis of farnesol. The main intermediate product of this synthesis – geranyl chloride – was obtained by two molecules starting from isoprene and acetopropyl alcohol respectively.

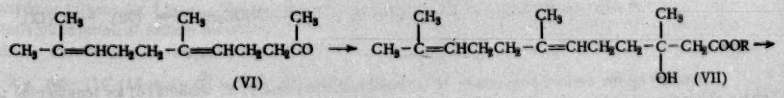
By the first method geranyl chloride was obtained from geraniol whose synthesis from isoprene we have already described [3].

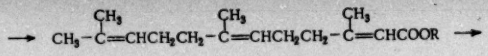
We now put forward a new method of preparation of geranyl chloride:



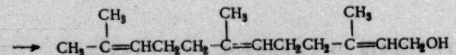
Acetoproply alcohol is converted via 2-methylpentanediol-2,5 (I) and 2,5-dibromo-2-methylpentane (II) into 5-bromo-2-methylpentene-2 (III) [4], which is then condensed with β-hydroxyethylmethyl ketone or methylvinyl ketone. The resultant 2,6-dimethyloctadien-2,7-ol-6, i.e. linalool (IV), is transformed by the action of thionyl chloride or hydrogen chloride into geranyl chloride (V).

The subsequent route of the synthesis of farnesol (IX) includes the following steps:





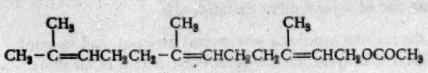
(VIII)



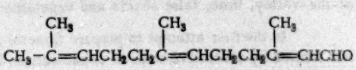
(IX)

α,β-Dihydropseudoionone (VI) is obtained by known method by condensation of geranyl chloride (V) with acetoacetic ester. Condensation of (VI) with ethyl chloroacetate in presence of magnesium gives ethyl farnesolate (VIII) which is reduced to farnesol (IX) with lithium aluminum hydride.

Treatment of the synthesized farnesol with acetyl chloride in presence of pyridine gave farnesyl acetate (X), while oxidation with activated manganese dioxide gave farnesal (XI):



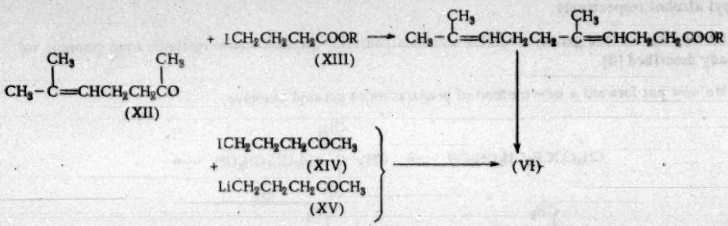
(X)



(XI)

Like farnesol, farnesyl acetate and farnesal are valuable perfume ingredients. We have thus achieved a complete synthesis of farnesol and farnesal without using natural compounds as starting substances.

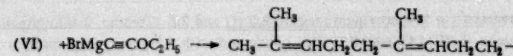
We may also point out that we have studied a more direct method of preparation of α,β-dihydro-pseudoionone(VI) involving condensation of 2-methylhepten-2-one (XII) with ethyl γ-iodobutyrate (XIII) of γ-iodopropylmethyl ketone (XIV) of γ-lithium-propylmethyl ketone (XV):

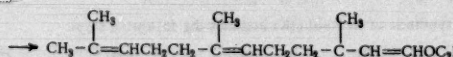


(XII) (XIII) (XIV) (XV) (VI)

As had been expected, in all these variants the yields were low (maximum 20%) due to the existance of numerous possibilities of other directions of the reaction. It was not always possible to isolate the required intermediate from the mixture of condensation products. In all cases, however, the end product, α,β-dihydropseudoionone (VI), was identical with the α,β-dihydropseudoionone obtained from geranyl chloride and acetoacetic ester.

We also effected the conversion from α,β-dihydropseudoionone (VI) to farnesol (IX) by the following route:





(XVI) (XI) (IX).

Employing the method proposed by N. A. Preobrazhensky and V. V. Shokina [5] for lengthening the chain of ketones and aldehydes by the group >CH−CHO with the help of ethoxyacetylenemagnesium bromide,

we condensed α,β-dihydropseudoionone (VI) with ethoxyacetylenemagnesium bromide and obtained, via the corresponding intermediate β-substituted vinyl ether (XVI), farnesal (XI) in a total yield of 47% reckoned on (VI). The melting point of the semicarbazone of the so-prepared farnesal did not give a depression in a mixed test with the semicarbazone of farnesal obtained by oxidation of farnesol. Farnesal was almost quantitatively reduced to farnesol (IX) with lithium aluminum hydride. This method is less convenient since it includes a selective hydrogenation step.

EXPERIMENTAL

2-Methylpentadiol-2,5 (I). To the Grignard reagent (cooled to 0°), prepared from 47.42 g magnesium and 278 g methyl iodide, was added dropwise in the course of 2 hours 88 g γ-acetopropyl alcohol (b.p. 117–119° at 43 mm) dissolved in 100 ml anhydrous ether. The mixture was stood for 8 hours at room temperature, then decomposed with crushed ice and neutralized with 20% acetic acid. The upper layer was collected and the aqueous layer was saturated with sodium chloride and repeatedly extracted with ethyl acetate. The residue after removal of the solvent was distilled in vacuum to give 52.42 g (51.4%). Viscous, light-yellow liquid with a characteristic odor.

B.p. 126–127° (16 mm), d_4^{20} 0.9645, n_D^{20} 1.4492, MR_D 32.89; Calcd. 32.96.

Found %: C 61.06; H 11.82. $C_6H_{14}O_2$. Calcd. %: C 60.98; H 11.94.

2,5-Dibromo-2-methylpentane (II). Into 21.2 g 2-methylpentanediol-2,5 in 50 ml anhydrous benzene was run, while cooling with iced water, in the course of 40 minutes, 40.6 g phosphorus tribromide dissolved in 40 ml anhydrous benzene. The reaction mass was then heated for 3 hours on a water bath. The unreacted phosphorus tribromide was decomposed with crushed ice. The upper layer was separated and washed with a little water until neutral; the aqueous layer was neutralized with saturated sodium bicarbonate solution and extracted with benzene. The solvent was distilled off from the combined extracts and the residue distilled in vacuum to give 24.56 g (56.1%). Colorless liquid, rapidly darkening in the light, with a pleasant odor.

B.p. 94–95° (40 mm), d_4^{20} 1.5400, n_D^{20} 1.4888, MR_D 45.72. $C_6H_{12}Br_2$. Calcd. 45.44.

5-Bromo-2-methylpentene-2 (III). A mixture of 23.8 g 2,5-dibromo-2-methylpentane and 7.8 g pyridine was heated for 2 hours in a low vacuum (150 mm) to 60–70°. The reaction mass was cooled and filtered. The precipitate was thoroughly washed with anhydrous ether. The solvent was distilled off and the residue distilled in vacuum to give 12.16 g (76.4%). Colorless liquid with a pleasant odor; rapidly darkens in the light.

B.p. 96° (100 mm), d_4^{20} 1.2172, n_D^{20} 1.4720, MR_D 37.54. $C_6H_{11}Br$. Calcd. 37.21.

2,6-Dimethyloctadien-2,7-ol-6 (linalool) (IV). Into 1.2 g magnesium covered with 10 ml anhydrous ether was run dropwise a solution of 8 g 5-bromo-2-methylpentene-2 10 ml anhydrous ether. The reaction was started by heating the mixture on a water bath. To the reaction product (cooled to 0°) was added in the course of 30 minutes 3.43 g methylvinyl ketone dissolved in 40 ml anhydrous ether. After stirring for 2 hours at room temperature, the reaction mass was decomposed with crushed ice and 20% acetic acid (litmus test). The upper layer was then collected and the aqueous layer extracted with ether. The residue after removal of the solvent was distilled in vacuum.

Yield 2.2 g (29.3%). Colorless liquid with a pleasant floral odor.

B.p. 128–130° (20 mm), d_4^{20} 0.8724, n_D^{20} 1.4625, MR_D 48.64; Calcd. 48.97.

Found %: C 77.52; H 11.99. $C_{10}H_{18}O$. Calcd. %: C 77.87; H 11.76.

Geranyl chloride (V). Dry hydrochloric acid was passed through a boiling solution of 100 g linalool in 30 ml anhydrous toluene for 2 hours. The reaction mass was then cooled to room temperature and neutralized with a saturated solution of sodium bicarbonate. The upper layer was collected. The residue after distillation of the toluene was distilled in vacuum. Yield 98 g (87.5%). Colorless liquid with a characteristic pleasant odor.

B.p. 105–110° (17 mm), d_4^{20} 0.9315, n_D^{20} 1.4799, MR_D 52.65; Calcd. 52.31.

Found %: C 69.31; H 9.68. $C_{10}H_{17}Cl$. Calcd. %: C 69.55; H 9.92.

α,β-Dihydropseudoionone (VI). Into sodium ethoxide, prepared from 11.73 g sodium and 200 ml anhydrous ethyl alcohol, was run in the course of half an hour 66.37 g freshly distilled acetoacetic ester (b.p. 110° at 80 mm). After 1 hour, 88.08 g geranyl chloride was added at the rate of 24–30 drops per minute and the mass was heated on a water bath until neutral (to litmus). 150 ml distilled water was then run in to dissolve the sodium chloride formed. This was followed by 42.9 g barium hydrate and the mixture was boiled 8 hours. The precipitated barium salt of geranyl-acetoacetic ester was treated with 20% hydrochloric acid until weakly acid (to litmus). The upper layer was separated and the lower layer extracted with ether. The solvent was driven off from the combined extracts. The residue was distilled in vacuum. Yield of α,β-dihydropseudoionone 78.9 g (79.6%).

B.p. 136–138° (10 mm), d_4^{20} 0.8812, n_D^{20} 1.4690, MR_D 61.41; Calcd. 61.31.

Found %: C 80.52; H 11.13. $C_{18}H_{32}O$. Calcd. %: C 80.34; H 11.41.

Ethyl ester of β-hydroxyhydrofarnesolic acid (VII). Into 4.86 g magnesium in 10 ml boiling anhydrous benzene was run a mixture of 38.86 g α,β-dihydropseudoionone and 24.4 g ethyl chloroacetate (b.p. 82° at 100 mm) dissolved in 20 ml anhydrous benzene. After addition of one-third of the solution, the start of reaction was expected. Further addition was made at a speed such that the mixture boiled gently. The reaction mass was afterwards boiled for an hour, and after cooling to 0° it was decomposed with 10% acetic acid. The benzene layer was separated and the aqueous layer extracted with benzene. The combined extracts were neutralized with saturated aqueous sodium bicarbonate solution. The residue after removal of the solvent was distilled in vacuum: b.p. 163–170° at 12 mm. Determination of active hydrogen by the Chugaev – Tserevitinov method showed that dehydration takes place during the reaction. Without further purification, the substance was used for preparation of the ethyl ester of farnesolic acid.

Ethyl ester of farnesolic acid (VIII). Into a solution of 6.7 g partially dehydrated ethyl ester of β-hydroxydihydrofarnesolic acid (VII) in 40 ml anhydrous benzene was run dropwise a mixture of 2.5 g phosphorus oxychloride and 16 ml pyridine. The reaction mixture was boiled 45 minutes, and after cooling it was run into water. The separated benzene layer was neutralized with saturated aqueous sodium bicarbonate solution. The solvent was distilled off and the residue distilled in vacuum. Yield 4.5 g.

B.p. 162–164° (10 mm), d_4^{20} 0.9230, n_D^{20} 1.4792, MR_D 81.25; Calcd. 80.96.

Found %: C 77.42; H 10.40. $C_{17}H_{28}O_2$. Calcd. %: C 77.21; H 10.67.

Farnesol (IX). To an ethereal solution (cooled to −50°) containing 0.38 g lithium aluminum hydride was added 2.6 g ethyl ester of farnesolic acid in 10 ml anhydrous ether and the mixture stirred 1 hour at −30°. The excess of lithium aluminum hydride was then carefully decomposed with water. The precipitate was filtered and thoroughly washed with ether. The filtrate was extracted with ether. The residue after driving off the solvent was distilled in vacuum. Yield 1.84 g (84.0%). An oily, light-yellow liquid with a characteristic floral odor when heavily diluted with alcohol.

B.p. 142–143° (2 mm), d_4^{20} 0.9016, n_D^{20} 1.4887, MR_D 71.21; Calcd. 71.59.

Found %: C 80.63; H 11.34. $C_{15}H_{26}O$. Calcd. %: C 81.02; H 11.79.

Farnesyl acetate (X). In a three-necked flask, fitted with stirrer, reflux condenser and dropping funnel and protected against atmospheric moisture by a calcium chloride tube, were placed 1.8 g farnesol, 10 ml anhydrous benzene and 10 ml dry pyridine. Addition was made, with ice cooling and stirring, of a solution of 0.64 g acetyl chloride in 5 ml anhydrous benzene. The reaction mass was stirred for 8 hours (ice cooling) and then decomposed with crushed ice. The upper layer was collected and the lower layer extracted with benzene. The benzene extracts were added to the collected layer and the mixture washed with 1% sulfuric acid and with saturated aqueous sodium bicarbonate solution. The benzene was driven off and the residue distilled in vacuum. Yield 1.5 g (70.1%).

B.p. 105–107° (2 mm), d_4^{20} 0.9247, n_D^{20} 1.4770, MR_D 80.79; Calcd. 80.96.

Found %: C 77.14; H 10.68. $C_{17}H_{28}O_2$. Calcd. %: C 77.21; H 10.67.

Farnesal (XI). 1.33 g farnesol, 100 ml ligroine (b.p. 60–80°) and 10 g activated manganese dioxide were placed in a bottle with a ground-glass stopper. The mixture was shaken 4 hours. The precipitate of manganese dioxide was filtered and washed several times on the filter with ligroine. The filtrate was dried

with calcined sodium sulfate, the solvent was driven off and the residue distilled in vacuum. Yield 9.8 g (62.1%). Faintly colored liquid with a pleasant floral odor.

B.p. 105–106° (3 mm), d_4^{20} 0.8999, n_D^{20} 1.4871. MR_D 70.46; Calcd. 70.08.

Found %: C 81.49; H 11.11. $C_{15}H_{24}O$. Calcd. %: C 81.77; H 10.97.

Semicarbazone: m.p. 136–137°.

SUMMARY

1. The complete synthesis of farnesol was accomplished.

2. Farnesol was oxidized to farnesal.

3. A new synthesis of linalool was described.

LITERATURE CITED

[1] M. Kerschbaum, Ber., 46, 1732 (1913).

[2] L. Ruzicka, Helv. Chim. Acta, 6, 483 (1923).

[3] G. I. Samokhvalov, M. A. Miropolskaya, L. A. Vakulova and N. A. Preobrazhensky, Proc. Acad. Sci. USSR, 84, 1179 (1952).

[4] L. Willimann and H. Schinz, Helv. Chim. Acta, 35, 2401 (1952).

[5] N. A. Preobrazhensky and V. V. Sholina, J. Gen. Chem., 15, 65 (1945).

Received October 27, 1954

Moscow Institute of Fine Chemical Technology

ACONITE ALKALOIDS

V. THE STRUCTURE OF THE CARBON SKELETON OF ZONGORINE

A. D. Kuzovkov

The aminoketone oxoaconitane was previously prepared [1] from zongorine by substitution by hydrogen of the two hydroxyl groups and reduction of the double bond of zongorine; this ketone was transformed into an oxygen-free compound – aconitane – by reduction of the keto group and substitution by hydrogen of the resultant hydroxyl.

Continuing the investigation, we have studied the Hofmann degradation of aconitane. Decomposition of aconitane methoiodide gave des-N-methylaconitane. Cleavage of des-N-methylaconitane methoiodide might have been expected to give a nitrogen-free substance since the single nitrogen atom of aconitane has a tertiary character, is located in the ring and is linked to an N-alkyl group. Instead, however, des-N-methylaconitane was obtained. This result leads to the hypothesis that a quaternary carbon atom is present in aconitane and zongorine in the β-position to the nitrogen; this would account for the impossibility of cleavage of the amino group during Hofmann degradation of des-N-methylaconitane methoiodide. For confirmation of this hypothesis, the N-alkyl group of oxoaconitane was substituted by hydrogen and the dehydrogenation with palladized carbon of the resultant secondary amine was studied. In presence of a quaternary carbon atom in the heterocycle, aromatization of the latter ought not to be realizable under relatively mild conditions. In fact, at 250–300° the evolution of hydrogen was not observed. This not only confirms the hypothesis of the presence of a quaternary carbon in the heterocycle of zongorine, but – if we take into consideration N. D. Zelinsky's discovery [2] of the stability to dehydrogenating catalysis of derivatives of cyclohexane containing quaternary carbon atoms in the rings – it also indicates the presence of quaternary carbon atoms in all the six-membered carbon rings of the molecules of oxoaconitane and zongorine.

For elucidation of the nature of the carbon skeleton of zongorine, the latter was subjected to selenium dehydrogenation at 320–340°. From the products of reaction could be isolated an aromatic hydrocarbon (I) whose composition approaches most closely to the formula $C_{18}H_{18}$. The ultraviolet absorption spectrum of (I) (in alcohol) is similar to the spectra of trisubstituted alkylphenanthrenes which are differentiated from the mono- and dialkylderivatives by a shift of the absorption bands toward the long-wave region and by smoothing and disappearance of some bands in the 320–350 mμ region [3].

In the table are presented the positions of the absorption maxima (magnitudes of $\lambda_{max.}$), and also the intensities of absorption (magnitudes of log ε) of the spectra of (I), 1,2,7-and 1,2,8-trimethylphenanthrenes [3]. It is readily seen that the spectrum of (I) differs from the spectra of 1, 2, 7 – and 1,2,8-trimethylphenanthrenes to no greater extent than the spectra of the two latter substances differ from one another. Such a similarity is convincing evidence that (I) is a phenathrene hydrocarbon apparently containing three alkyl groups.

TABLE

1. Hydrocarbon from zongorine	$\lambda_{max.}$	260	282	292	304	322	334	346	–
	$\lg \varepsilon$	4.74	4.13	4.02	4.08	2.51	2.50	2.28	–
2. 1,2,7-Trimethylphenanthrene	$\lambda_{max.}$	260	283	291	302	322	337	–	353
	$\lg \varepsilon$	4.82	4.18	4.08	4.10	2.60	2.71	–	2.60
3. 1,2,8-Trimethylphenanthrene	$\lambda_{max.}$	261	283	295	307	323	339	347	354
	$\lg \varepsilon$	4.77	4.07	4.08	4.19	2.62	2.54	2.30	2.18

A comparison of the properties of (I) with those of known phenanthrene hydrocarbons reveals the similarity between the constants of (I) and its complex compounds with those of 1-ethyl-2-methylphenanthrene.

However, a direct comparison of (I) with 1-ethyl-2-methylphenanthrene prepared by us by the known method [4] pointed to a difference between the two substances.

Out of the number of hydrocarbons isolated up to now by dehydrogenation of aconite alkaloids, (I) most resembles the hydrocarbon of unknown structure from napelline [5] ($C_{19}H_{18}$, m.p. 76–79°; picrate m.p. 132–134°; complex with trinitrobenzene m.p. 150–153°).

On the basis of the investigations it can be concluded that part of the hydrocarbon skeleton of zongorine is the hydrogenated nucleus of phenanthrene containing quaternary carbon atoms in all three rings; the nitrogen atom is in the β-position to a quaternary carbon atom. Some of these properties of zongorine are evidently also common to other alkaloids of the atisine group; as we know, the method of dehydrogenation with selenium has been applied to the study of atisine, hetisine, napelline and staphysine; in all these cases phenanthrene hydrocarbons were obtained (phenanthrene, 1,7-dimethylphenanthrene, 1-methyl-6-ethylphenanthrene and 1,3-dimethyl-7-isopropylphenanthrene). It has been suggested [6] that atisine contains a quaternary carbon atom in the heterocycle on the basis of the observation that the heterocyclic ring is not aromatized on dehydrogenation of atisine with selenium.

EXPERIMENTAL

Aconitane methoiodide. 0.75 g aconitane in 20 ml methanol was boiled 12 hours with 5 ml methyl iodide, with addition each 2 hours of methyl alcoholic alkali to give a weakly alkaline reaction (to phenolphthalein). The aconitane methoiodide was extracted with chloroform from the dry residue after removal of the CH_3OH and CH_3I. Yield 0.95 g, m.p. 244° (from a mixture of alcohol and ether). Ether did not extract any bases from the aqueous solution after making alkaline (test for absence of hydroiodide).

Found %: I 27.86. $C_{22}H_{36}NI$. Calcd. %: I 28.82.

Des-N-methylaconitane. 0.9 g aconitane methoiodide and 45 ml 30% methyl alcoholic potassium hydroxide were boiled 2 hours under reflux. After evaporation, addition of water to the residue and extraction with ether, the des-N-methylaconitane was obtained in a yield of 0.5 g, m.p. 109–110° (from acetone). Hydrochloride of des-N-methylaconitane, m.p. 266–267° (from a mixture of alcohol and ether).

Found %: C 84.74; H 11.01; N 4.46. $C_{22}H_{35}N$. Calcd. %: C 84.28; H 11.25; N 4.47.

Des-N-methylaconitane methoiodide. The reaction was effected under the same conditions as for aconitane methoiodide. From 0.4 g des-N-methylaconitane was obtained 0.35 g methoiodide, m.p. 257–258° (from a mixture of alcohol and ether); after its aqueous solution had been made alkaline, no bases were extracted with ether.

0.3 g des-N-methylaconitane methoiodide was boiled 2 hours with 15 ml 30% methyl alcoholic potassium hydroxide. The sole product of the reaction was a base with m.p. 110–111° (0.2 g), which did not give a depression with des-N-methylaconitane.

Noroxoaconitane. 4.2 g oxoaconitane and 1.8 g cyanogen bromide were heated 1 hour in a sealed tube at 100°; ether extraction of the products of reaction gave 4 g faintly colored liquid cyanamide, insoluble in acids and alkalies. The cyanamide was heated 6 hours with 40 ml 30% alcoholic potassium hydroxide; the residue after distillation of the alcohol was dissolved in water; the solution was acidified with 20% hydrochloric acid and repeatedly extracted with ether. After drying and evaporation of the ether extract to a small volume, 2.4 g crystalline substance with m.p. 245–246° (from alcohol) was obtained; judging by its analysis this was the product of incomplete hydrolysis of the cyanamide.

Found %: C 73.44; H 8.63; N 8.24. $C_{20}H_{28}O_2N_2$. Calcd. %: C 74.09; H 8.29; N 8.23.

2.1 g substance with m.p. 245–246° and 150 ml 30% H_2SO_4 were refluxed; then from a dropping funnel was slowly added a solution of 0.9 g $NaNO_2$ in 20 ml H_2O. After cooling, the solution was made alkaline with concentrated aqueous ammonia and extracted with ether. There was obtained 1.2 g noroxoaconitane, b.p. 180–190° (1 mm), m.p. 125–127°, sublimes at 120° (0.1 mm).

Found %: C 80.64; H 9.61; N 4.57. $C_{19}H_{27}ON$. Calcd. %: C 79.96; H 9.51; N 4.91.

Noroxoaconitane hydrochloride, m.p. 257–258° (from a mixture of alcohol and ether). Benzoylnoroxoaconitane. 0.6 g noroxoaconitane, 0.6 g benzoyl chloride and 10 ml anhydrous pyridine were boiled

2 hours, the pyridine was driven off in vacuum, and the dry residue was extracted with ether. The ethereal solution was extracted successively with 10% HCl, 10% NaOH and water, then dried and evaporated to a small volume to give 0.5 g benzoylnoroxoaconitane, m.p. 164–165.5° (from a mixture of ether and acetone). The compound is insoluble in acids and alkalies.

Found %: C 80.44; H 8.57; N 3.49. $C_{24}H_{31}O_2N$. Calcd. %: C 79.56; H 8.28; N 3.71.

Dehydrogenation of zongorine with selenium. 14 g zongorine and 14 g selenium were heated in a nitrogen atmosphere for 8 hours at 320–340°. A benzene extract of the reaction mass was obtained and purified by shaking with 10% H_2SO_4, 5% NaOH and water; it was then evaporated to give 6 g resinous residue, part of this residue was soluble in ligroine (4 g) and was chromatogrammed on 150 g Al_2O_3 from ligroine (b.p. 60–80°); on washing with the same solvent; a moving zone fluorescing strongly in ultraviolet light was observed. When this zone approached the bottom of the column, the washing was stopped, the descending solvent was removed by a weak vacuum. The lower, fluorescing part of the sorbate was separated and eluted with ether to give about 1 g yellowish oil from which was obtained a picrate, weight 0.8 g after crystallization from alcohol, m.p. 125–126°. On passing the ethereal solution of the picrate through Al_2O_3 and evaporating the eluate, 0.4 g hydrocarbon was obtained. It was again chromatogrammed on 150 ml Al_2O_3 from a mixture of ligroine and benzene (10:1); washing was effected with the same solvent. The fluorescent zone of the column was divided into 4 parts; the two middle parts (washed out with ether) gave a crystalline hydrocarbon (0.12 g); after the fifth crystallization from methanol it formed colorless needles with m.p. 80.5–81.5°; this melting point did not change after a sixth crystallization.

Found %: C 92.85, 92.52; H 7.64, 7.92. $C_{18}H_{18}$. Calcd. %: C 92.27; H 7.74.

To a warm alcoholic solution of 10 mg of the hydrocarbon (m.p. 78.5–79.5°) was added 10 mg picric acid; about 20 mg picrate was obtained; after drystallization from alcohol the m.p. was 134–134.5°; vivid orange needles; no change in melting point after recrystallization.

Found %: C 62.35, 62.18; H 4.55, 4.65: $C_{69}H_{18} \cdot C_6H_3O_7N_3$. Calcd. %: C 62.20; H 4.57.

5 mg hydrocarbon (m.p. 80.5–81°) and 5 mg styphnic acid were dissolved in alcohol by heating; on cooling a styphnate with m.p. 152–153° came down; no change in m.p. on recrystallization.

7 mg hydrocarbon (m.p. 78.5–79.5°) and 7 mg trinitrobenzene were dissolved in alcohol by heating; a substance with m.p. 154.5–155.5° came down on cooling; after recrystallization from alcohol the m.p. was 155–156°.

SUMMARY

A study was made of the Hofmann degradation of aconitane, of the dehydrogenation with palladium of the prepared (for the first time) noroxoaconitane, and of the dehydrogenation of zongorine with selenium.

The hypothesis was advanced that part of the carbon skeleton of zongorine is the hydrogenated nucleus of phenanthrene containing quaternary carbon atoms in all the rings; the nitrogen atom is in the β-position to a quaternary carbon atom.

LITERATURE CITED

[1] A. D. Kuzovkov, J. Gen. Chem., 23, 504 (1953) (T.p. 521)*

[2] N. D. Zelinsky, Selected Works, II, Moscow-Leningrad, 58, 112, 124 (1941).

[3] F. A. Askew, J. Chem. Soc., 1935, 509.

[4] R. D. Haworth, C. R. Mavin and G. Sheldrick, J. Chem. Soc., 1934, 454.

[5] W. A. Jacobs and L. C. Craig, J. Biol. Chem., 143, 611 (1942).

[6] O. E. Edwards and Singh Tara, Chemistry and Industry, N 47, 1258, (1953).

Received November 1, 1954

S. Ordzhonikidze Scientific Research Institute of Pharmaceutical Chemistry

* T.p. = C. B. Translation pagination.

ALKALOIDS OF THE SPECIES HAPLOPHYLLUM A. JUSS. II

S. Yu. Yunusov and G. P. Sidyakin

The preceding paper [1] reported an investigation of the varieties of Haplophyllum A. Juss. (family of the Rutaceae) growing in Central Asia. A study was made of the qualitative and quantitative changes of the ala alkaloids in various organs of the plants of this species in dependence on the locality of growth and the period of vegetation [2].*

The alkaloid haplophine $C_{13}H_{11}O_3N$, that we isolated from H. pedicellatum, has m.p. 140–141° and contains two methoxyl groups; its formula may therefore be written: $C_{11}H_5ON(OCH_3)_2$. This is reminiscent of the alkaloid γ-fagarine (4,8-dimethoxy-2,3-furanoquinoline), isolated from the leaves of the Argentine plant Fagara Coco (family of the Rutaecae) [3–5].

Not having at our disposal a sample of γ-fagarine for direct comparison, we carried out with haplophine a series of reactions general for furanoquinolinic alkaloids [6, 7].

On heating the base with methyl iodide in a sealed tube to 100°, an iso compound is formed with m.p. 176–177° which contains one methoxyl group less than the original base. Oxidation of haplophine with potassium permanganate gives an aldehyde with the composition $C_9H_4ON(OCH_3)_2CHO$ with m.p. 186–187° and an acid with the composition $C_9H_4ON(OCH_3)_2COOH$ with m.p. 215–216°. Heating of the acid with 30% hydrochloric acid causes decarboxylation and demethylation at the expense of one methoxyl group with formation of a compound $C_9H_6O_2N(OCH_3)$, m.p. 250–251°. By subjecting the product to further oxidation with potassium permanganate in an aqueous medium, we succeeded in isolating an acid with the composition $C_6H_3(NH_2)(OCH_3)$ COOH with m.p. 162–163°, which was identified as 3-methoxyanthranilic acid.

A comparison of the melting points of the products of breakdown of haplophine with the corresponding products of γ-fagarine readily shows their identity (Table 1); the name of "γ-fagarine" must therefore be retained for our base.

TABLE 1
Melting points of haplophine, γ-fagarine and their breakdown products

Substance	Haplophine	γ-Fagarine
Base	140–141°	139–140°
Iso compound	176–177	179
Aldehyde	186–187	185
Acid	215–216	215
Product of decarboxylation	250–251	250

In the same way supplementary confirmation was obtained about the alkaloid skimmianine [1, 8] isolated by us from several varieties of Haplophyllum.

The next subject of our investigations was the perennial Haplophyllum dubium Eug. Kor. [9]. This plant was gathered in the vicinity of the village of Gazarak in the Sary-Assiya region of the Surkhandarinsk oblast of Uzbekistan. Collection was made during the budding stage and at the start of flowering of the plant (9th to 16th June).

Isolation of the alkaloids from the leaves in admixtures with some fine stalks, buds and flowers was effected by extraction with dichloroethane. The acid solution was made alkaline with gaseous ammonia and the alkaloids were extracted with ether and then with chloroform.

From the ethereal extract was obtained a crystalline base to which we gave the name of dubinine. This has the composition $C_{16}H_{17}O_5N$ and gives a crystalline methoiodide, nitrate and hydrochloride. Dubinine does not contain an N-alkyl group; one atom of oxygen is in the form of methoxyl, a second in the form of hydroxyl; two atoms are in the form of a methylenedioxy group. The remaining oxygen atom is indifferent in character. The formula of dubinine must accordingly be : $C_{14}H_{11}ON(OCH_3)(OH)(CH_2O_2)$.

* All the plants that were chemically studied by us were collected and studied botanically by a special expedition led by E. E. Korotkova.

Treatment with methanol of the mixture of alkaloids of the chloroform extract gave an additional amount of dubinine. The total yield of dubinine was 0.06% of the dry weight of the leaves.

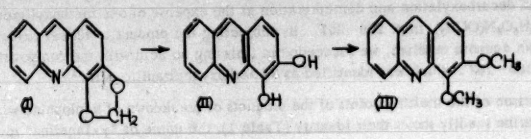
The alkaloids remaining in the mother liquor form a yellow crystalline mixture of hydrochlorides with dilute hydrochloric acid. These were converted to the bases from which, exploiting the differing solubility in ligroine, could be isolated two more alkaloids. We named one of these (colorless) dubinidine, and the other (light-yellow) dubamine.

Dubinidine forms a crystalline methoiodide, hydrochloride, nitrate and picrate. Elementary analysis leads to the formula $C_{19}H_{17}O_4N$; since a methoxyl group and a methylenedioxy group are present, the formula may be written: $C_{11}H_{12}ON(OCH_3)(CH_2O_2)$. The fourth oxygen has an indifferent character.

With aqueous and alcoholic hydrochloric acid, dubamine gives a yellow hydrochloride; with nitric acid it gives a yellow nitrate. The only substituent group in dubamine is the methylenedioxy group. The elementary composition corresponds to the formula $C_{14}H_9O_2N$ or to the more detailed formula: $C_{13}H_7N(CH_2O_2)$. If we imagine the latter to have two hydrogen atoms in place of the methylenedioxy group, we have acridine $C_{13}H_9N$. Consequently it may be suggested that dubamine is methylenedioxyacridine.

For confirmation of this hypothesis, the methylenedioxy ring in the dubamine molecule was opened by the action of phloroglucinol and concentrated hydrochloric acid in a sealed tube [10]. In this way dubamine was completely transformed into a phenolic substance with m.p. 212–214° (II). Treatment of this phenol with diazomethane gave an ether with m.p. 187–188° (III); the picrate of the latter has m.p. 216–218°.

The above constants agree with the constants reported in the literature for the dimethyl ether of 3,4-dihydroxyacridine and its picrate [11]. Since in our case the substances were obtained by opening of the methylenedioxy ring, we can assume with a high degree of probability that dubamine has the structure of 3,4-methylenedioxyacridine (I):



As a supplement to the above facts, we present in Table 2 data fro the contents of alkaloids in the varieties of Haplophyllum that we studied. Determinations were carried out by the method of continuous extraction of the alkaloids with chlorofrom followed by extraction with sulfuric acid. The aqueous solution was made alkaline with ammonia and the alkaloids were extracted with chloroform; the latter was distilled off to leave the total bases.

The data submitted in Table 2 for eleven varieties of Haplophyllum indicate that the alkaloids are mainly in the leaves during the flowering period.

Attention is merited by the shrub Haplophyllum foliosum Vved., containing 2% alkaloids in the leaves. From the total bases of this plant we were able to isolate two pure alkaloids. One of them was skimmianine, the other dubinidine. Consequently this is the fourth variety of Haplophyllum containing skimmianine, and the second variety containing dubinidine (Table 3).

EXPERIMENTAL

1. Isolation of total alkaloids from Haplophyllum dubium. 40 kg air-dry, pulverized leaves with admixture of some fine stalks, buds and flowers was wetted with 8% ammonia solution and percolated with dichloroethane. The alkaloids were extracted from the dichloroethane extract with 10% sulfuric acid. After making alkaline with ammonia, the aqueous solution was shaken with ether and then with chloroform. From the ether extract was obtained 25 g, and from the chloroform extract 60 g of total alkaloids (0.21%).

2. Dubinine. The crystalline residue from the ether extract was recrystallized 5 times from methyl alcohol (1:5) and then from ethyl alcohol (1:15).• The colorless crystals (small needles) of dubinine had m.p. 185–186°. Yield 20 g. Dubinine is soluble in acetone and pyridine; it is insoluble in ligroine, water and alkalies.

$[\alpha]_D^0$ −73.1° (c 0.864; acetone).

Found %: C 63.15, 63.48; H 5.93, 6.19; N 4.55, 4.62; OH 5.28, 5.87 (Tserevitinov); CH_3O 10.46, 10.15. $C_{16}H_{17}O_5N$. Calcd. %: C 63.35; H 5.64; N 4.61; OH 5.6; CH_3O 10.22.

Nitrate. To a solution of 1 g base in 5 ml chloroform was added dropwise a solution of 3 drops concentrated nitric acid in 5 ml chloroform until the reaction was acid to congo. On adding ether the nitrate crystallizes with m.p. 123–124°. Yield 1 g. After 3 crystallizations from acetone (1:15), m.p. 148–150° (frothing).

Found %: N 7.42, 7.79. $C_{16}H_{17}O_5N \cdot HNO_3$. Calcd. %: N 7.64.

Hydrochloride. 6.5 g base was mixed with 10 ml 5% hydrochloric acid. The hydrochloride was collected and washed with water. Yield 7 g. After 3 recrystallizations from water (1:5), m.p. 170–171°. Addition of 5% ammonia solution to an aqueous solution of the hydrochloride brings down the original base.

Found %: Cl 10.7, 10.3. $C_{16}H_{17}O_5N \cdot HCl$. Calcd. %: Cl 10.43.

Methoiodide. A mixture of 0.5 g base with 1 ml methyl iodide in a sealed tube was heated on a boiling water bath 30 minutes. At first the substance dissolved and later crystallization commenced. On cooling, the entire mass crystallized. The tube was opened and the residue of methyl iodide distilled off. Yield 1 g. The methoiodide crystallizes from methanol (1:7), m.p. 211–212°.

Found %: N 3.33, 3.27; CH_3O 6.96, 6.82; I 28.33, 28.70. $C_{16}H_{17}O_5N \cdot CH_3I$. Calcd. %: N 3.17; CH_3O 6.96; I 28.5.

3. Alkaloids of the chloroform extract. Dubinidine. 60 g alkaloid mixture of the chlorofrom extract was triturated with 100 ml methanol. The insoluble dubinine (3 g) was separated and the solvent was completely distilled off from the mother liquor. To the residue was added 5% hydrochloric acid until the reaction was acid to congo. The yellow, crystalline precipitate of hydrochlorides was filtered and washed with cold water. Yield 22 g. The mixture of hydrochlorides was dissolved in warm water. It was made alkaline with ammonia. The precipitated bases were dried and boiled with ligroine (5 times with 100 ml each time). The insoluble residue (12 g) was recrystallized 3 times from acetone (1:100). Colorless needles of dubinidine were obtained with m.p. 132–133°; readily soluble in ethyl alcohol, more difficultly soluble in chloroform and ether, insoluble in ligroine and water.

Found %: C 61.88, 61.87; H 6.49, 6.43; N 5.40, 5.49; CH_3O 10.62, 10.21. $C_{15}H_{17}O_4N$. Calcd. %: C 62.15; H 6.77; N 5.58; CH_3O 12.3.

Hydrochloride. 0.65 g base was dissolved in 3 ml alcoholic hydrochloric acid. On cooling, 0.75 g dubinidine hydrochloride came down with m.p. 194–195°. After recrystallization from water (1:10) m.p. 195–196°. Decomposition of the hydrochloride with ammonia regenerates the base.

Nitrate. To a solution of 0.5 g base in 3 ml alcohol was added dropwise concentrated nitric acid until the reaction was acid to congo. Ether was added to bring down the crystals of nitrate. The latter is readily soluble in methanol, alcohol and water. After 3 recrystallizations from acetone (1:140) m.p. 176–177°.

The picrate is formed by mixing an ethereal solution of 0.1 g base with an ethereal solution of 0.12 g picric acid. After recrystallization from alcohol m.p. 155–156°.

Methoiodide. A mixture of 0.2 g base and 0.25 ml methyl iodide in a sealed tube was heated on a boiling water bath 3 hours. After the tube had been opened the residue of methyl iodide was distilled off, and the product recrystallized from water. M.p. of the methoiodide 153–154°.

Found %: CH_3O 7.57, 7.57. $C_{15}H_{17}O_4N \cdot CHI$. Calcd. %: CH_3O 7.88.

• The residual mother liquor was combined with the chloroform extract.

TABLE 2

Content of alkaloids in some varieties of Haplophyllum A. Juss.

Variety	Region where collected	Period of vegetation	% content of alkaloids	
			in the leaves	in the stalks
H. perforatum	Kitab, Uzbek SSR	Before budding	0.1	–
		Budding	0.1	0.14
		Flowering	0.4	0.1
		Fruit-bearing*	1.2	0.075
H. pedicellatum	Kitab, Uzbek SSR	Flowering	0.3	–
		Fruit-bearing	0.4	–
H. dubium	Sary-Assiya, Uzbek SSR	Flowering**	0.23	0.04
H. popovii	Kurgan-Tyube, Tadzhik SSR	Flowering	0.16	–
H. latifolium	Brich-Mulla, Kazak SSR	Flowering	0.2	–
H. Bunge	Termez, Uzbek SSR	Flowering	0.1	0.04
H. robustum	Kelif, Uzbek SSR	Flowering	0.2	0.06
H. Alberti-Regelii	Kugitang, Turkmenian SSR	Flowering	0.07	0.05
H. foliosum	Stalinabad, Tadzhik SSR	Flowering	2.0	0.4
H. bucharicum	Dekhkanabad, Uzbek SSR	Flowering	Whole plant 0.11	
H. versicolor	Guzar, Uzbek SSR	Flowering	Above-ground part 0.011	

Dubamine. The ligroine extract was concentrated to a small volume. On cooling, yellow crystals of dubamine came down with m.p. 90–92°. After many recrystallizations from ligroine (1:5) and methanol (1:4) m.p. 96–97°. Dubamine has good solubility in ether, acetone and benzene; it is less soluble in alcohol, and insoluble in water.

Found %: C 75.03, 75.35; H 4.88, 4.30; N 5.86, 5.74. $C_{14}H_9O_3N$. Calcd. %: C 75.33; H 4.03; N 6.27.

Dubamine hydrochloride is formed by the action of 5% hydrochloric acid on the base. Yellow needles with m.p. 201–202° (from water).

Dubamine nitrate comes down when concentrated nitric acid is added to an alcoholic solution of the base until the reaction is acid to congo. Yellow needles from methanol, m.p. 157–158°.

4. Saponification of the methylenedioxy group of dubamine. Dihydroxyacridine. 0.6 g dubamine hydrochloride was well mixed with 1 g phloroglucinol and 15 ml hydrochloric acid (d 1.18). The mixture was heated in a sealed tube on an oil bath at 140–150° for 4 hours. With progressive heating the solution turned red and deposited an orange precipitate. After cooling, the mixture was diluted with 50 ml water and made alkaline with conc. NH_3; the base was then extracted with chloroform. After driving off the solvent, 0.5 g orange base of phenolic character was left, m.p. 212–214°; an alcoholic solution of the latter turned dark-green with ferric chloride. This base was readily soluble in acetone and ethyl and methyl alcohols, less soluble in ether and chloroform, poorly soluble in ligroine. It crystallizes from chloroform (1:50).

Dimethyl ether. A solution of 0.1 g dihydroxyacridine in 25 ml anhydrous ether was mixed with an ethereal solution of diazomethane prepared from 2 g methylurea. After 3 days the solvent was distilled off. The residual yellow oil was dissolved in 3 ml alcohol, and to the solution was added a few drops of water.

* In the seeds 1.6%, in the roots 0.025%.

** In the roots 0.04%.

TABLE 3

Alkaloids of plants of the species Haplophyllum A.Juss.

Name of alkaloid	Gross formula	Detailed formula	Melting point		Producing plant	Content of alkaloid (in percent of weight of dry leaves)
			of base	of hydrochloride		
9 Skimmianine	$C_{14}H_{13}O_4N$	$C_{11}H_4ON(OCH_3)_3$	176°	153–154°	H. perforatum	0.01–0.8
					H. pedicellatum	0.07
					H. bucharicum	–
					H. foliosum	–
10 γ-Fagarine	$C_{13}H_{11}O_3N$	$C_{11}H_5ON(OCH_3)_2$	140–141	250	H. pedicellatum	0.13
11 Haploperine	$C_{17}H_{19}O_6N$	$C_{15}H_{13}O_4N(OCH_3)_2$	155–156	129–131	H. perforatum	0.075
12 Dubinine	$C_{16}H_{17}C_5N$	$C_{14}H_{11}ON(OCH_3)(OH)(CH_2O_2)$	186	171–171	H. dubium	0.06
13 Dubinidine	$C_{13}H_{17}O_4N$	$C_{11}H_{12}ON(OCH_3)(CH_2O_2)$	132–133	195–196	H. dubium	0.03
					H. foliosum	
14 Dubamine	$C_{14}H_9O_2N$	$C_{13}H_7N(CH_2O_2)$	96–97	201–202	H. dubium	0.025
15 Base No. 2	–	–	151–152	–	H. bucharicum	–
16 Base No. 3	–	–	110–111	–	H. perforatum	–

The yellow precipitate of the dimethyl ether was collected and washed with dilute alcohol. After recrystallization from alcohol, m.p. 188–189°.

The picrate of the dimethyl ether was formed by the action of an alcoholic solution of picric acid. M.p. 217–218°.

SUMMARY

1. All the 11 varieties of Haplophyllum A. Juss. that we investigated contain alkaloids. Apparently the remaining varieties of this species are also alkaloid-bearing.

2. It was demonstrated that haplophine, isolated from Haplophyllum pedicellatum Bge., is identical with γ-fagarine.

3. Three alkaloids were isolated from the leaves of Haplophyllum dubium Eug. Kor.:

dubinine $C_{16}H_{17}O_5N-C_{14}H_{11}ON(OCH_3)(OH)(CH_2O_2)$,

dubinidine $C_{13}H_{17}O_4N-C_{11}H_{12}ON(OCH_3)(CH_2O_2)$ and

dubamine $C_{14}H_9O_2N-C_{13}H_7N(CH_2O_2)$.

4. The structure of 3,4-methylenedioxyacridine is considered extremely probable for dubamine.

LITERATURE CITED

[1] S. Yu. Yunusev and G. P. Sidyakin, Proc. Acad. Sci. USSR, 12, 15 (1950); J. Gen Chem., 22 1055 (1952). (T.p. 1103)•

[2] S. Yu. Yunusev, Bull. Acad. Sci. Uzbek SSR, 4, 11 (1948).

[3] G. V. Stuckert, Chem. Zentr., 1934, 1, 67.

[4] V. Deulofeu, R. Labriola and J. Lange, J. Am. Chem. Soc., 64, 2326 (1942).

[5] B. Berinzaghi, A. Maruzabal, R. Labriola and V. Deulofeu, J. Org. Chem., 10, 181, (1945).

[6] V. Asahina, T. Ohtau. and M. Inubuse, Ber., 63, 2045 (1930).

[7] V. Asahina and M. Inubuse, Ber., 63, 2052 (1930).

[8] J. Honda, Chem. Zentr., 1904, II, 1511

[9] Flora USSR, XIV, Publishing House of the Academy of Sciences USSR, 200 (1949).

[10] Clowes and Tolens, Ber., 32, 2841 (1899); Weber and Tolens, Ann. chim., 299, 316 (1898).

[11] Dict. Org. Compounds, 1, 814 (1949).

Received December 15, 1954

Institute of Chemistry of the Academy of Sciences of the Uzbek SSR

• T.p. = C. B. Translation pagination.